



Institute for Reference
Materials and Measurements



CERTIFICATION REPORT

**Certification of the mass fractions of As, B, Cd, Cr, Cu,
Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn in rye grass**

Certified Reference Material ERM[®]-CD281

EUR 24363 EN – 2010

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Certification of the mass fractions of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn in rye grass

Certified Reference Material ERM[®]-CD281

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Summary

This report describes the preparation and certification of the rye grass Certified Reference Material (CRM) ERM-CD281. This CRM replaces the exhausted predecessor BCR-281. ERM-CD281 was processed and certified by the European Commission, Directorate General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

ERM-CD281 has been certified for its content of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn.

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

The following values were assigned:

| Element | Mass Fraction | |
|--|--|--------------------------------------|
| | Certified value ¹⁾ [mg/kg] | Uncertainty ²⁾ [mg/kg] |
| As | 0.042 | 0.010 |
| B | 5.5 | 0.5 |
| Cd | 0.120 | 0.007 |
| Cr | 24.8 | 1.3 |
| Cu | 10.2 | 0.5 |
| Hg | 0.0164 | 0.0022 |
| Mn | 82 | 4 |
| Mo | 2.22 | 0.12 |
| Ni | 15.2 | 0.6 |
| Pb | 1.67 | 0.11 |
| Sb | 0.042 | 0.007 |
| Se | 0.023 | 0.004 |
| Sn | 0.062 | 0.011 |
| Zn | 30.5 | 1.1 |
| <p>1) The value is the unweighted mean of accepted sets of data, each set being obtained in a different laboratory and/or with a different method. The certified values are reported on dry mass basis and are traceable to the SI.</p> <p>2) Expanded uncertainty with a coverage factor $k = 2$ according to the Guide to the Expression of Uncertainty in Measurement (GUM), corresponding to a level of confidence of about 95 %.</p> | | |

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Glossary

| | |
|-----------------------|---|
| AAS | Atomic Absorption Spectrometry |
| AFS | Atomic Fluorescence Spectrometry |
| ANOVA | Analysis of variance |
| BCR | Community Bureau of Reference |
| CC | Collision cell |
| CCT | Collision Cell Technology |
| CRMs | Certified Reference Materials |
| CV-A-AFS | Cold Vapour Atomic Fluorescence Spectrometry with Gold Amalgamation |
| CV-AAS | Cold Vapour Atomic Absorption Spectrometry |
| CV-AFS | Cold Vapour Atomic Fluorescence Spectrometry |
| DMA | Direct Mercury Analyzer |
| DRC | Dynamic Reaction Cell |
| ERM [®] | Trade mark of European Reference Materials |
| ET-AAS | Electrothermal Atomic Absorption Spectrometry |
| FAAS | Flame Atomic Absorption Spectrometry |
| HG-AFS | Hydride Generation Atomic Fluorescence Spectrometry |
| HR | High resolution |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectrometry |
| ICP-QMS | Inductively Coupled Plasma Quadrupole Mass Spectrometry |
| ICP-SFMS | Inductively Coupled Plasma Sector Field Mass Spectrometry |
| ID | Isotope dilution |
| IRMM | Institute for Reference Materials and Measurements |
| ISO | International Organization for Standardization |
| k | Coverage factor |
| k_0 -INAA | k_0 -Instrumental Neutron Activation Analysis |
| k_0 -NAA | k_0 -Neutron Activation Analysis |
| LR | Low resolution |
| wt. % | Weight percentage |
| MR | Medium resolution |
| MS_{between} | Mean squares between-bottle from an ANOVA |
| MS_{within} | Mean squares within-bottle from an ANOVA |
| n | Number of replicates per vial |
| n_{ns} | Number of measurements on normal stock samples |
| n_{ref} | Number of measurements on reference samples |
| N/A | Not applicable |
| n.c. | Not calculated |
| NIST | National Institute of Standards and Technology |
| QC | Quality Control |
| RM Unit | Reference Materials Unit |

| | |
|----------------------|---|
| RNAA | Radiochemical Neutron Activation Analysis |
| RSD | Relative Standard Deviation |
| s | Standard deviation |
| s_{bb} | Between-bottle standard deviation |
| $s_{bb, rel}$ | Between-bottle relative standard deviation |
| s_{ns} | Standard deviation of results of normal stock samples |
| s_{ref} | Standard deviation of results of reference samples |
| SI | International System of Units |
| u_{bb} | Standard uncertainty related to a possible between-bottle heterogeneity |
| $u_{bb, rel}$ | Relative standard uncertainty related to a possible between-bottle heterogeneity |
| u_{bb}^* | Standard uncertainty related to a maximum heterogeneity that could be hidden by method repeatability |
| $u_{bb, rel}^*$ | Relative standard uncertainty related to a maximum heterogeneity that could be hidden by method repeatability |
| u_{char} | Standard uncertainty of the material characterisation |
| $u_{char, rel}$ | Relative standard uncertainty of the material characterisation |
| u_{rec} | Standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution |
| $u_{rec, rel}$ | Relative standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution |
| U_{CRM} | Expanded uncertainty of the certified value |
| $U_{CRM, rel}$ | Expanded relative uncertainty of the certified value |
| u_{lts} | Standard uncertainty of the long-term stability |
| U_{meas} | Expanded measurement uncertainty |
| $\nu_{MS_{within}}$ | Degrees of freedom of MS_{within} |
| V-KFT | Volumetric Karl Fischer titration |
| t_{sl} | Proposed shelf life |
| \bar{x} | Average of all results of the homogeneity study |
| $\overline{x_{ns}}$ | Average of all results of normal stock samples |
| $\overline{x_{ref}}$ | Average of results of reference samples |
| x_i | Time point for each replicate |

1 Introduction

Animal feed quality has a significant impact on the quality of the food products derived from animals and thus on human health and is one of work areas of the EU legislation, e.g. Regulation (EC) No 1831/2003, Directive 2001/22/EC and Directive 2002/32/EC. There are several elements of high importance owing to their nutritional or toxic properties [1, 2]. Elements such as B, Cu, Cr, Mg, Mn, K, Ni, P, Se, Sn and Zn are classified as elements of nutritional quality. However, their dietary role depends on their content in animal feed. Too high intakes of a nutrient can cause toxic effects. The tolerance limit of the nutrient depends both on the animal species and on their diet composition. A number of important nutritional and biochemical interactions between feed components have been recognised. For instance, Cu metabolism is strongly related to the Mo content, and coexistence of vitamin E and Se provide protection against metals such as Cd, Hg, As or Pb. It becomes clear that the information about the content of nutritional elements in animal feed helps to design a well-balanced diet for animals.

On the other hand, examples of elements, which represent a potential risk for human or animal health are As, Cd, Hg and Pb. In order to avoid negative effects on the health of domestic animals, the detection of this kind of elements is necessary. Failure to detect these elements could lead to a lower production (economic loss) or cause damage to the health of consumers of animal products (milk, meat, cheese, etc.). Some elements such as Sb are more often found in the environment because of human activities. Since they can play significant role for human and animal health in the future, their precise and careful control in feed is required. The measurement of some of the elements (e.g. Pb or Cd) is also relevant for the environmental monitoring and pollution control.

BCR-281 (Certified Reference Material for trace elements in rye grass) that was used in routine analysis of animal feed is out of stock. Therefore, ERM-CD281 Rye Grass certified for the total content of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn has been produced. This report describes the preparation and certification of the ERM-CD281.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE

(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE

(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)

2.3 Homogeneity and stability studies

ALS Scandinavia AB, Luleå, SE

(accredited to ISO/IEC 17025 for element determination in environmental matrices and food, SWEDAC No 1087)

Helmholtz Zentrum München - Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), Neuherberg, DE

Studiecentrum voor Kernenergie - Centre d'Etude de l'énergie Nucléaire (SCK-CEN), Mol, BE

(accredited to ISO/IEC 17025 for element determination in animal feed, sediment and soils using k_0 -NAA, BELAC No 015-TEST)

The Food and Environment Research Agency (FERA), York, GB

(accredited to ISO/IEC 17025 for element determination in animal feed and soils, UKAS No 1642)

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, BE

(accredited to ISO/IEC 17025 for measurement of elements in soils, BELAC No 045-TEST)

2.4 Characterisation

ALS Scandinavia AB, Luleå, SE

(accredited to ISO/IEC 17025 for element determination in environmental matrices and food, SWEDAC No 1087)

Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, DE

(accredited to ISO/IEC 17025 for measurement of trace elements in foodstuffs, DAP-PL-2614.14)

DSM Resolve, Geleen, NL

Energieonderzoek Centrum Nederland (ECN), Petten, NL

(accredited to ISO/IEC 17025 for element determination in plants, sediment and ash, RVA No L135)

Helmholtz Zentrum München - Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), Neuherberg, DE

Minton, Treharne & Davis Limited, Carmarthenshire, GB

(accredited to ISO/IEC 17025 for element determination in environmental matrices and food, UKAS No 1946)

Institut "Jozef Stefan" (JIS), Ljubljana, SI

Laboratoire National de métrologie d'Essais (LNE), Paris, FR

(accredited to ISO/IEC 17025 for element determination in food and sediments, COFRAC No 2-54)

LGC Limited, Teddington - Middlesex, GB

(accredited to ISO 17025/IEC for measurement of trace elements in food, inorganic and organic matrices, UKAS No 0003)

MTT Agrifood Research Finland, Jokioinen, FI

(accredited to ISO/IEC 17025 for measurement of elements in food and feed, FINAS T024)

Studiecentrum voor Kernenergie - Centre d'Etude de l'énergie Nucléaire (SCK-CEN), Mol, BE

(accredited to ISO/IEC 17025 for element determination in animal feed, sediment and soils using k_0 -NAA, BELAC No 015-TEST)

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(accredited to ISO/IEC 17025 for element determination in plants and sewage sludge, BMWA No -92.714/0518-I/12/2007)

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VA SYD, Malmö, SE

(accredited to ISO/IEC 17025 for element determination in sewage sludge and sediments, SWEDAC No 2011)

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, BE

(accredited to ISO/IEC 17025 for measurement of elements in soils, BELAC No 045-TEST)

3 Processing of the material

The rye grass used for ERM-CD281 was harvested in 1983 [3-5]. In 1988-1989, one part became the now sold-out BCR-281 and another part BCR-129 [3-5]. Some of the remaining material was processed by jet milling in 1994 and thereafter made available in 25 g portions [6]. The finely ground powder from 1994 was further processed at IRMM in 2006. The further processing consisted of drying at 50 °C (to reach the water content below 4 wt. %), homogenisation, filling into amber 60 mL glass vials with a lyo-insert and an aluminium cap under argon atmosphere. Capping and labelling was performed according to the filling sequence. A total of 2422 units were produced, each containing about 10 g of the rye grass material.

The particle size distribution of the final product was assessed using a Sympatec Helos laser diffraction instrument (Clausthal-Zellerfeld, DE). A typical particle size distribution is presented in Figure 1. The maximum particle size was shown to be 175 µm. However, a sieve analysis demonstrated presence of larger particles of 200 µm - 3 mm, see Figure 2 (d). In relation to the total number of particles, their relative abundance is much below 1 %.

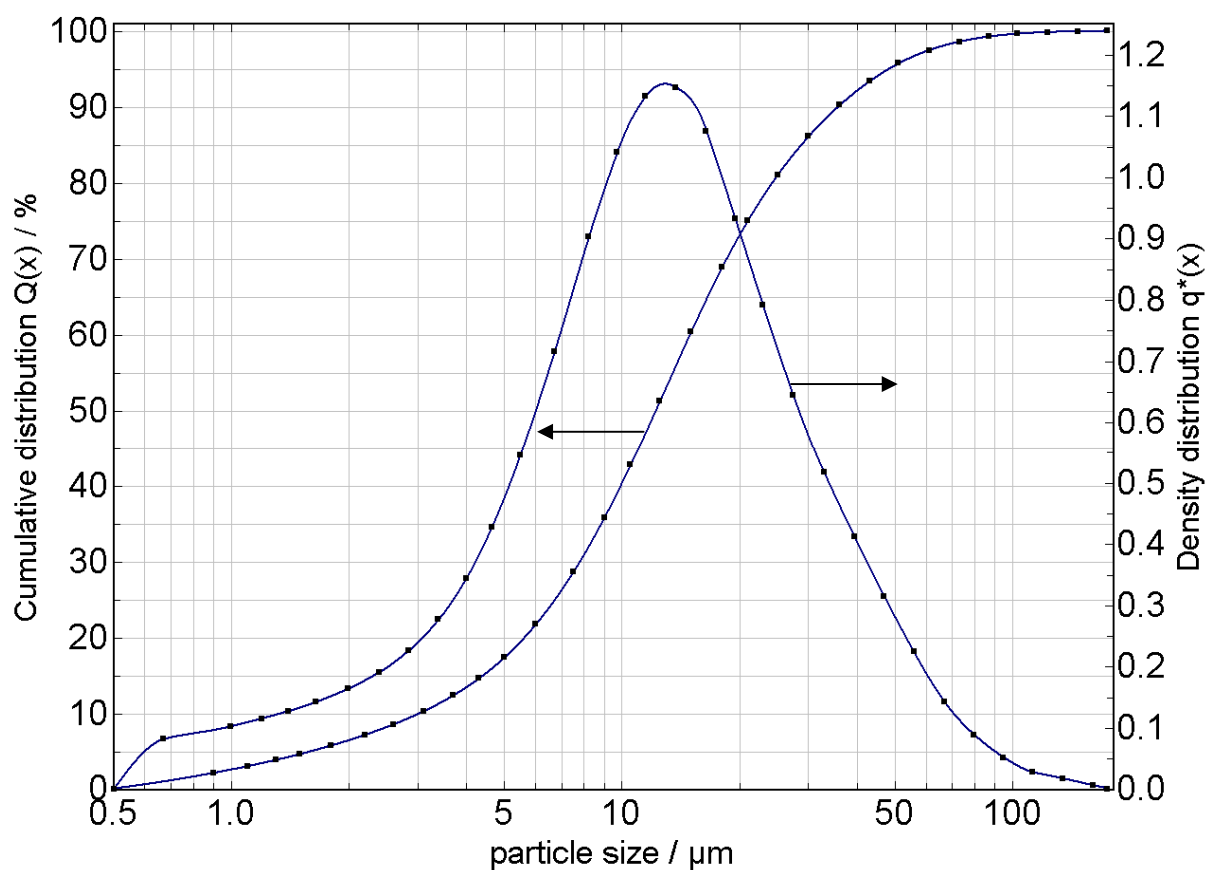


Figure 1: Typical particle size distribution of ERM-CD281 (average of triplicate measurements on three vials). Instrument: Sympatec Helos laser diffraction instrument (Clausthal-Zellerfeld, DE), optical concentration: 15 % - 25 % using the cuvette, and dispersant: 2-propanol.

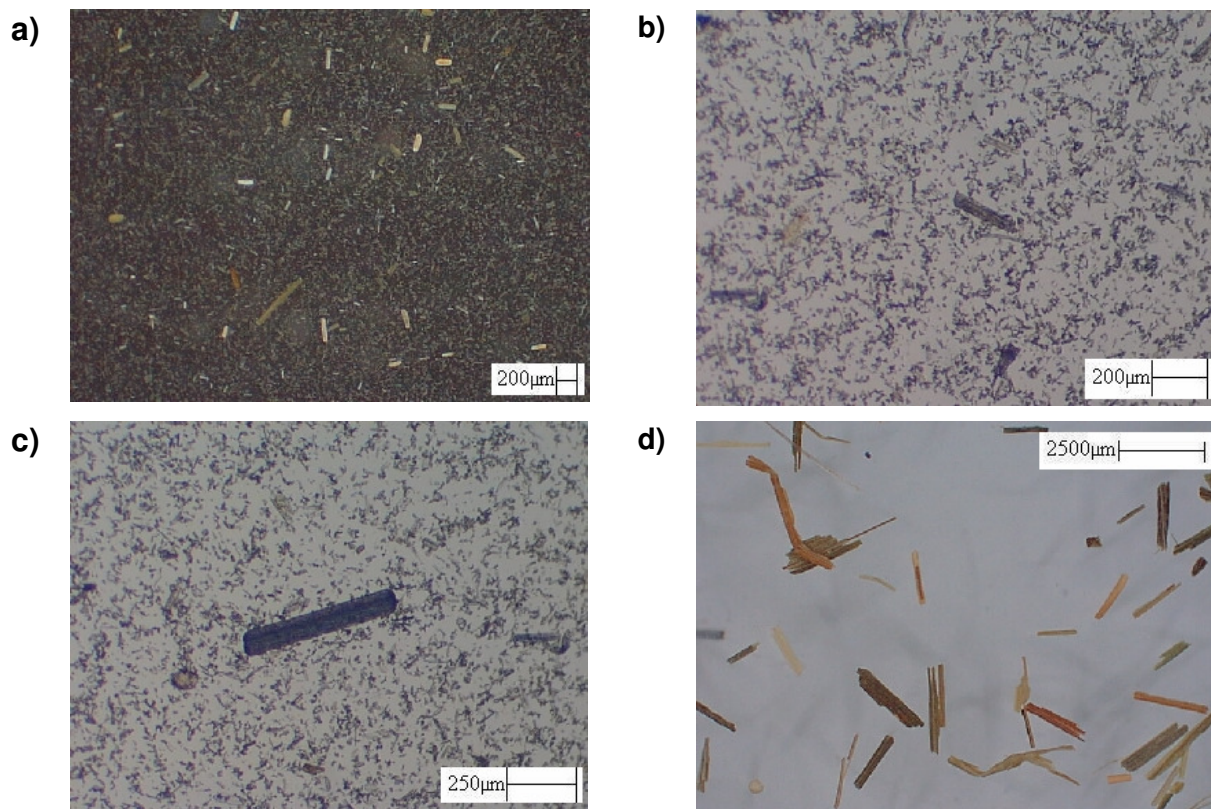


Figure 2: Micrographs of the final product, ERM-CD281 (a – c), and micrograph of the particles remaining on a 250 µm sieve after sieve analysis of ERM-CD281 (d).

The water content determined in the final product using volumetric Karl Fischer titration (V-KFT, Metrohm Ltd, Herisau, CH) was 2.68 wt. % \pm 0.30 wt. % (average of triplicate measurements on ten vials, expanded uncertainty with a coverage factor of $k = 2$). The water content was also monitored by high speed Acousto-Optical Tunable Filter Near Infrared Spectrometry (AOTF-NIR) during capping of the vials. As shown in Figure 3 the water content over the whole batch was constant. The few observed outliers were associated with a bad ratio of the signal to the noise.

The water activity determined in the final product by means of a water activity meter (Aqualab CX3, Decagon, USA) was 0.107 (average of triplicate measurements on one vial).

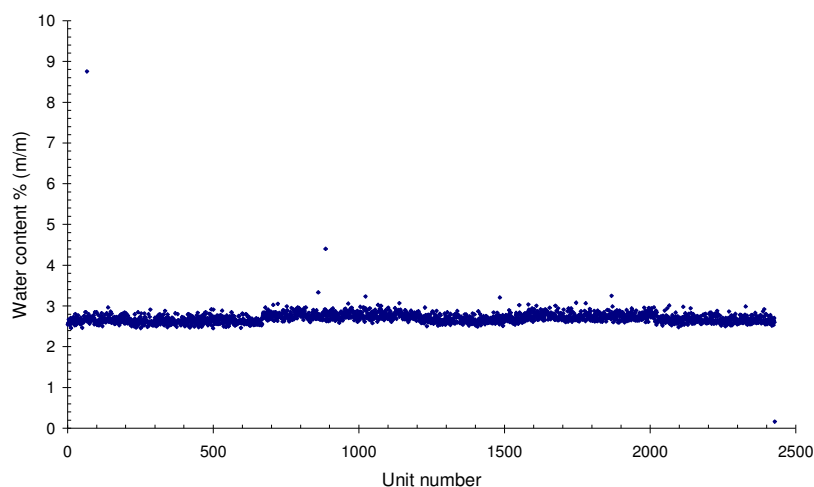


Figure 3: Results of the water content monitoring during capping of ERM-CD281. The visibly outlying data are due to a bad ratio of the signal to the noise.

4 Homogeneity

4.1 Between-bottle homogeneity

The between-bottle homogeneity was evaluated to ensure that the certified values of the CRM are valid for all vials of the material, within the stated uncertainty.

For the homogeneity test, fifteen vials were selected using a random stratified sampling scheme. The number of selected vials corresponds to approximately the cubic root of the total number of the produced units. The batch was divided into fifteen groups (with similar number of vials) and one vial was randomly selected from each group.

From each vial, three samples were prepared by digestion in a microwave oven using 5 mL HNO₃ and 0.5 mL HCl. The samples were analysed by means of ICP-OES (B, Cr, Cu, Mn, Mo, Ni and Zn), ICP-SFMS (MR: As and LR: Cd, Hg, Pb, Sb and Sn) and ICP-QMS with NH₃ DRC (Se). The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results were corrected for the water content determined in each vial once (see Section 6.2).

In case of As, Hg and Se it turned out that the homogeneity results were not in agreement with those from the characterisation exercises (about 10, 2 and 10 times higher, respectively). Based on some further investigations the laboratory confirmed these findings giving interference problems as an explanation. In case of As applying too low mass resolution could be a reason as well. Therefore, the homogeneity results for those elements were not used and the material homogeneity was evaluated using data from the short-term stability study (this approach is correct when no influence for the conditions tested in the stability study is present, as shown in Section 5.1). This resulted in a dataset with measurements on fourteen vials. The vials were analysed in triplicate by means of ICP-SFMS (HR: As and Se) and CV-AFS (Hg) after digestion in a microwave oven using 6 mL HNO₃ and 2 mL HCl. The measurements were performed under repeatability conditions, and in a randomised manner. The results were corrected for the water content determined in each vial twice (see Section 6.2).

The results of these measurements were evaluated using a method described by Linsinger *et al.* [7] as described in the following paragraphs:

The obtained data were first tested whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms (if the data do not follow at least a unimodal distribution, the calculation of standard deviations would be inappropriate). All individual results were normally and unimodally distributed.

Grubbs-tests were performed to detect potentially outlying individual results as well as outlying vial averages. Some outlying individual results and outlying vial averages for both homogeneity and stability results were found, see Annex A (homogeneity) and Table 3 (outlying individual values in stability measurements). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Furthermore, regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence were visible. However, some trends in the analytical sequence were visible, pointing at instability of the analytical system (As, Cd, Cu, Mn, and Sn). Since the uncertainty of homogeneity was very low for Cd, Cu and Mn (see Table 1), and in case of As and Sn the drift correction would not significantly affect the uncertainty, the drift correction was not applied.

The results were then evaluated by a one-way analysis of variance (ANOVA). From the results of the ANOVA calculation, the following figures were determined:

Between-bottle standard deviation (s_{bb}) as given by:

$$s_{bb} = \sqrt{\frac{MS_{\text{between}} - MS_{\text{within}}}{n}}, \quad (1)$$

where:

MS_{between} : mean squares between-bottle from an ANOVA
 MS_{within} : mean squares within-bottle from an ANOVA
 n : average number of replicates per vial

The maximum heterogeneity that can be hidden by the method repeatability (which is used as the minimum uncertainty contribution from homogeneity) defined by:

$$u_{bb}^* = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt[4]{\frac{2}{v_{MS_{\text{within}}}}}, \quad (2)$$

where:

$v_{MS_{\text{within}}}$: degrees of freedom of MS_{within}

The larger value of s_{bb} or u_{bb}^* was used as uncertainty contribution from the homogeneity, u_{bb} . However, a different approach was adopted for As and Pb for which one outlying vial average was detected. In this case between-bottle heterogeneity was modelled as a rectangular distribution limited by the largest outlying vial average, and the rectangular standard uncertainty of homogeneity was estimated as given by:

$$u_{\text{rec}} = \frac{|\text{largest outlying vial average} - \bar{x}|}{\sqrt{3}}, \quad (3)$$

where:

\bar{x} : average of all results of the homogeneity study

However, it should be mentioned that the outlying vial averages are a result of presence of outlying individual values and do not necessarily reflect the real distribution of these elements in the material.

The results of the measurements are shown in Annex A (homogeneity study) and D (long-term stability study). The results of the evaluation of the between-bottle variation are summarised in Table 1. In most cases, the uncertainty contribution for homogeneity was determined by the method repeatability.

Table 1: Results of the homogeneity study

| Element | $S_{bb, \text{rel}}$ [%] | $U_{bb, \text{rel}}^*$ [%] | $U_{\text{rec, rel}}$ [%] | $U_{bb, \text{rel}}$ [%] |
|-----------------|--|-------------------------------|------------------------------|-----------------------------|
| As ^b | N/A | N/A | 9.4 | 9.4 |
| B ^a | 0.4 | 0.8 | | 0.8 |
| Cd ^a | n.c. | 0.8 | | 0.8 |
| Cr ^a | 0.6 | 0.5 | | 0.6 |
| Cu ^a | n.c. | 0.6 | | 0.6 |
| Hg ^b | 3.3 | 1.8 | | 3.3 |
| Mn ^a | 0.5 | 0.4 | | 0.5 |
| Mo ^a | n.c. | 1.4 | | 1.4 |
| Ni ^a | 0.7 | 0.6 | | 0.7 |
| Pb ^a | N/A | N/A | 2.3 | 2.3 |
| Sb ^a | n.c. | 1.5 | | 1.5 |
| Se ^b | n.c. | 3.4 | | 3.4 |
| Sn ^a | n.c. | 2.9 | | 2.9 |
| Zn ^a | 0.3 | 0.3 | | 0.3 |
| n.c.: | cannot be calculated as $MS_{\text{between}} < MS_{\text{within}}$ | | | |
| a: | based on the data from the dedicated homogeneity study | | | |
| b: | based on the data from the short-term stability study | | | |
| N/A | not applicable | | | |

The potential between-unit variation is generally below 1 – 3 %. Some exceptions were noted for As (9.4 %), Hg (3.3 %) and Se (3.4 %). The high value for As is a result of presence of the outlier. This between-unit variation is small enough compared to the method variability usually observed (average up to 10 % was obtained by the participants of the characterisation measurements for these three elements). This material is therefore sufficiently homogeneous to be suitable as reference materials.

4.2 Minimum sample intake

The minimum sample intake is the minimum amount of sample that is representative for the whole unit thus can be used in an analysis. Samples equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

To estimate of the minimum sample intake series of measurements with decreasing amount of sample for one randomly selected vial were performed. The following sample intakes were tested: 200 mg, 100 mg and 50 mg. For each sample intake 6 samples were prepared by digestion in a microwave oven using 3 mL HNO₃. Each sample intake was prepared in one independent microwave run. All the samples were analysed together by means of ICP-QMS (B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Sn and Zn) and ICP-SFMS (HR: As and Se) under repeatability conditions, and in a randomised manner. The measurement method was robust over the whole range of the sample intake tested and its repeatability was in the same range or below the repeatability achieved during the material characterisation (see Section 6).

The obtained data sets (all sample intakes taken together) were first tested whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms (if the data do not follow at least a unimodal distribution, the calculation of standard deviations is doubtful or impossible). All results were normally and unimodally distributed.

Furthermore, the results (all sample intakes taken together) were scrutinised for outliers using single Grubbs-test. One outlier for Cu was found. This outlier was significant on a 95 %, but not on a 99 % confidence level. Since no technical reason for the outlier could be found, the result was retained. In any case, its removal would not affect results of the minimum sample intake determination.

The minimum sample intake was established by comparison of variances obtained for 100 mg and 50 mg sample intakes with the variance obtained for 200 mg sample intake. It was done using F-test for equality of two samples for variances with degrees of freedom of 5 and a confidence level of 95 %.

The obtained results are presented in Annex B and the minimum sample intakes are summarised in Table 2.

Table 2: Results of the minimum sample intake determination

| Element | Minimum sample intake [mg] |
|---------|-------------------------------|
| As | 50 |
| B | 100 |
| Cd | 200 |
| Cr | 50 |
| Cu | 200 |
| Hg | 50 |
| Mn | 100 |
| Mo | 100 |
| Ni | 100 |
| Pb | 50 |
| Sb | 200 |
| Se | 100 |
| Sn | 50 |
| Zn | 100 |

As shown above, the minimum sample intake representative for all elements is 200 mg. However, lower sample intakes can be also applied, i.e. 100 mg for As, B, Cr, Hg, Mn, Mo, Ni, Pb, Se, Sn and Zn and 50 mg for As, Cr, Hg, Pb and Sn.

5 Stability

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, quite high temperatures can be reached. The stability studies have been carried out using an isochronous design [8]. In that approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"). At the end of the isochronous storage the samples are analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests. Time, temperature and light (UV-radiation) were regarded as the most relevant influences on stability of the material. The influence of UV-radiation was minimised by the choice of a brown glass vials, which eliminate most of the incoming light. In addition, materials are stored and dispatched in the dark, thus practically eliminating the possibility of degradation by UV-radiation. Therefore, only the influences of time and temperature needed to be investigated. Elements are not subject to thermal degradation at temperatures encountered during everyday life. However, it is known that some organometallic compounds have a low boiling point, e.g. tetracarbonyl nickel. Moreover, if an element is certified for its mass fraction, degradation of the matrix would affect this mass fraction as well. Therefore, assessment of the material stability under certain temperature and time conditions was required.

5.1 Short-term stability study

For the short-term stability study, samples have been stored at 18 °C and 60 °C for 0, 1, 2 and 4 weeks (at each temperature). The reference temperature was set to -20 °C. Two samples per storage time were selected using a random stratified sampling scheme. From each vial, three samples were prepared by digestion in a microwave oven using 5 mL HNO₃ and 0.5 mL HCl (exception: for 60 °C test temperature, 1 week storage time only two samples were prepared from one vial). All samples were analysed with respect to the content of all elements by means of ICP-OES (B, Cr, Cu, Mn, Mo, Ni, Zn,) ICP-SFMS (MR: As, and LR: Cd, Hg, Pb, Sb and Sn) and ICP-QMS with NH₃ DRC (Se). The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the water content determined in each vial once (Section 6.2).

Similarly to the homogeneity study, the results for As, Hg and Se were not in agreement with those of the material characterisation (see Section 6). Therefore, additional measurements for those elements have been carried out. A new set of samples was analysed in triplicate by means of ICP-SFMS (HR: As and Se) and CV-AFS (Hg) after digestion in a microwave oven using 6 mL HNO₃ and 2 mL HCl. The measurements were performed under repeatability conditions, and in a randomised manner. The results were corrected for the water content determined in each vial twice (Section 6.2).

The obtained data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. Some outlying individual results were found (see Table 3). As no technical reason for the outliers could be found all data were retained for statistical analysis.

Furthermore, the data were plotted against storage time and the regression lines were calculated. The slope of the regression lines was then tested for statistical significance (loss/increase due to shipping conditions). For all elements, the slopes of the regression lines were not significantly different from 0 (on 95 % and 99 % confidence level) for both 18 °C and 60 °C.

The results of the measurements are shown in Annex C. The results of the evaluation of the material short-term stability are summarised in Table 3.

Table 3: Results of the short-term stability tests

| Element | Number of individual outlying results | | Measurement technique | Significance on 95 % and 99% confidence level | |
|---------|---------------------------------------|----------------|-----------------------|---|-------|
| | 18 °C | 60 °C | | 18 °C | 60 °C |
| As | 1 ^a | 0 | ICP-SFMS | No | No |
| B | 0 | 0 | ICP-OES | No | No |
| Cd | 0 | 0 | ICP-SFMS | No | No |
| Cr | 0 | 0 | ICP-OES | No | No |
| Cu | 1 ^b | 0 | ICP-OES | No | No |
| Hg | 0 | 0 | CV-AFS | No | No |
| Mn | 0 | 0 | ICP-OES | No | No |
| Mo | 0 | 1 ^b | ICP-OES | No | No |
| Ni | 0 | 0 | ICP-OES | No | No |
| Pb | 0 | 0 | ICP-SFMS | No | No |
| Sb | 0 | 0 | ICP-SFMS | No | No |
| Se | 0 | 0 | ICP-SFMS | No | No |
| Sn | 0 | 1 ^b | ICP-SFMS | No | No |
| Zn | 0 | 0 | ICP-OES | No | No |

^a: on a 99 % confidence level

^b: on a 95 % confidence level

It was concluded that the material is stable at 18 °C and 60 °C for up to 4 weeks. The samples can be safely dispatched under conditions where the temperatures do not exceed 60 °C for up to 4 weeks, i.e. at ambient temperature.

Because the potential degradation due to dispatch can be considered negligible, the uncertainty contribution from the short-term stability is not considered in the estimation of the total uncertainty of the material (see Section 7.1).

5.2 Long-term stability study

For the long-term stability study, samples have been stored at 18 °C for 0, 4, 8 and 12 months (1-year study) and for 0, 8, 16 and 24 months (2-year study). The reference temperature was set to -20 °C. Two samples per each storage time were selected using a random stratified sampling scheme. From each vial, three samples were prepared by digestion in a microwave oven. As digestion reagents, 5 mL HNO₃ and 0.02 mL HF (5 mL HNO₃, 0.02 mL HF and 0.2 mL HCl for Sb and Sn) for the 1-year study samples were used. The 2-year study samples were digested with 6 mL HNO₃ and 2 mL HCl. The digests of 1-year study samples were analysed by means of ICP-SFMS (HR: As and Se; MR: Cr, Cu, Mn, Ni and Zn; LR: B, Cd, Hg, Mo, Pb, Sb and Sn). The digests of 2-year study samples were analysed by means of ICP-SFMS (HR: As and Se; MR: B, Cd, Mo, Pb, Sb, and Sn), ICP-OES (Cr, Cu, Mn, Ni and Zn) and CV-AFS (Hg). The measurements were performed

under repeatability conditions, and in randomised manner to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the water content determined in each vial twice (Section 6.2).

The measurements of As, Hg and Se (1-year study) were performed close to the method LOD. Therefore, the results were not used.

The data were tested for outliers using the single and double Grubbs test (each time-scheme was evaluated separately). A few outliers were found in both 1-year and 2-year studies (see Table 4). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Table 4: Outliers detected in the long-term stability measurements

| Element | Number of individual outlying values | |
|---------|--------------------------------------|----------------|
| | 1-year study | 2-year study |
| As | Not used | 1 ^a |
| B | 0 | 0 |
| Cd | 1 ^a | 0 |
| Cr | 0 | 0 |
| Cu | 0 | 2 ^a |
| Hg | Not used | 0 |
| Mn | 0 | 0 |
| Mo | 0 | 1 ^a |
| Ni | 0 | 0 |
| Pb | 0 | 0 |
| Sb | 2 ^a | 1 ^b |
| Se | Not used | 0 |
| Sn | 0 | 0 |
| Zn | 0 | 0 |

^a: on a 95 % confidence level

^b: on a 99 % confidence level

Furthermore, the data were plotted against time and the regression lines were calculated (each time-scheme was evaluated separately). The slope of the regression lines was then tested for statistical significance (loss/increase due to storage conditions). For Cd and Cr in the 1-year study the slopes of the regression line were found to be significant on 95 % and 99 % confidence level, respectively. This is caused by the data of the samples stored at only reference temperature, for which one data point for Cd and five for Cr were lower in comparison to the other storage times. Since these findings were not confirmed by the 2-year stability study, it was concluded that the slope significance is rather a result of measurement error and does not reflect a real element distribution in the material. Therefore, it was decided to exclude these results and not to use them in the material stability evaluation.

Finally, the results of the both stability schemes were combined and evaluated together. Since the two datasets were obtained using different analytical techniques and in different

time a correction had to be applied. The 1-year stability results were corrected by multiplying with a correction factor calculated from the ratio of the study averages. For most of the elements the correction factor was equal or less than 1.1 only for As and Hg higher factor had to be applied, i.e. 1.3 and 1.2, respectively. Therefore, for these elements only the 2-year study data were used to evaluate the material stability. Again, the data points were plotted against time and the regression lines were calculated. The slope of the regression lines was tested for statistical significance as well. Since all slopes were not significantly different from 0 on a both 95 % and 99% confidence level, the uncertainty contribution of the long-term stability, u_{Its} could be established as:

$$u_{\text{Its}} = \frac{s}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{\text{sl}}, \quad (4)$$

where:

- s : standard deviation of all results of the stability study
- x_i : time point for each replicate
- \bar{x} : average of all time points
- t_{sl} : proposed shelf life (24 months at 18 °C in this case)

When combining the stability data one degree of freedom was lost due to the correction applied. However, it was checked that this change has no impact on the uncertainty of stability and was therefore neglected.

The results of the evaluation of the material stability are summarised in Table 5. The results of the measurements are shown in Annex D.

Table 5: Results of the long-term stability tests

| Element | Measurement technique | Slope significance | $u_{\text{its, rel}}^a$ [%] | Source of data |
|---------|-----------------------|--------------------|-----------------------------|--|
| As | ICP-SFMS | No | 5.4 | 2-year stability study |
| B | ICP-SFMS | No | 1.5 | Combined 1-year and 2-year stability study |
| Cd | ICP-SFMS | No | 1.9 | 2-year stability study |
| Cr | ICP-OES | No | 0.9 | 2-year stability study |
| Cu | ICP-SFMS ICP-OES | No | 1.2 | Combined 1-year and 2-year stability study |
| Hg | CV-AFS | No | 2.8 | 2-year stability study |
| Mn | ICP-SFMS ICP-OES | No | 1.2 | Combined 1-year and 2-year stability study |
| Mo | ICP-SFMS | No | 1.3 | Combined 1-year and 2-year stability study |
| Ni | ICP-SFMS ICP-OES | No | 1.0 | Combined 1-year and 2-year stability study |
| Pb | ICP-SFMS | No | 1.2 | Combined 1-year and 2-year stability study |
| Sb | ICP-SFMS | No | 7.2 | Combined 1-year and 2-year stability study |
| Se | ICP-SFMS | No | 4.8 | 2-year stability study |
| Sn | ICP-SFMS | No | 6.4 | Combined 1-year and 2-year stability study |
| Zn | ICP-SFMS ICP-OES | No | 1.1 | Combined 1-year and 2-year stability study |

^a: established for a shelf life of 24 months at 18 °C

Since the characterisation exercise took longer than planned, it was required to check the material stability beyond the established 24 months shelf life. This was done by comparative analysis of 2 vials of the CRM stored at the normal storage temperature (18 °C) and 2 references samples (placed at -20 °C directly after the material processing). Freezing of the reference samples is assumed to render the material degradation negligible. All the samples were analysed (five replicates per each vial) by means of ICP-SFMS (HR: As and Se; MR: Cr, Cu, Mn, Ni and Zn; LR: B, Cd, Hg, Mo, Pb, Sb and Sn), after digestion in a microwave oven using 5 mL HNO₃ and 0.02 mL HF (5 mL HNO₃, 0.2 mL HCL and 0.02 mL HF for Sb and Sn). Additionally, triplicate measurements of Cr, Mn, Sb and Zn using k₀-INAA were performed. The results were corrected for the water content determined in each vial twice (see Section 6.2).

The obtained results of the normal stock samples (stored at 18 °C) were compared with the certified value (see Section 7) taking into account their uncertainties. The uncertainty of the dedicated measurements was established as standard deviation divided by square root of number of measurements, i.e. 10 for ICP-SFMS and 6 for k₀-INAA. For the certified value its expanded standard uncertainty ($k = 2$) was used (see Section 7).

Additionally, a comparison of normalised results was performed to check the correctness of the measurement methods. The normalisation was done as described below:

- the normal stock results were divided by the results obtained from analysis of the reference samples,
- the certified value was set to 1,
- the uncertainty of the certified value was its expanded standard uncertainty ($k = 2$), see Section 7,
- the expanded standard uncertainty of the dedicated measurements was established as:

$$U_{\text{meas}} = 2 \cdot \frac{\bar{x}_{\text{ns}}}{\bar{x}_{\text{ref}}} \cdot \sqrt{\left(\frac{\frac{s_{\text{ns}}}{\sqrt{n_{\text{ns}}}}}{\bar{x}_{\text{ns}}} \right)^2 + \left(\frac{\frac{s_{\text{ref}}}{\sqrt{n_{\text{ref}}}}}{\bar{x}_{\text{ref}}} \right)^2}, \quad (5)$$

where:

- U_{meas} : expanded standard measurement uncertainty with coverage factor, $k = 2$
- $s_{\text{ns}}, s_{\text{ref}}$: standard deviations of results of normal stock samples and reference samples, respectively
- $n_{\text{ns}}, n_{\text{ref}}$: number of results of normal stock samples and reference samples, respectively
- $\bar{x}_{\text{ns}}, \bar{x}_{\text{ref}}$: average of all results of normal stock samples and reference samples, respectively

All the results obtained using k_0 -INAA were in agreement with the certified values. The results obtained using ICP-SFMS were in agreement with the certified values with some exceptions: the reported data for Cd were below and for B, Cu, Mn above the uncertainty limit of the certified value. However, the values normalised to the reference samples were within the uncertainty of the certified value. This indicates a bias of the measurements or insufficient accuracy of the method used. Additional confirmation of this observation are the results of the k_0 -INAA method, that showed the stability of the material in case of Mn (Cd, B and Cu were not measured). Therefore, it was concluded that the material is stable with respect to the content of all tested elements and its shelf life can be extended for the next 24 months at 18 °C. After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

The results of the stability control are summarised in Annex E.

6 Characterisation

6.1 Approach

The material characterisation was based on a laboratory intercomparison approach, i.e. the element content in the material was determined in different laboratories that applied different measurement procedures to avoid method bias.

Participants for the characterisation study were selected based on criteria that comprised both technical and quality management aspects. Fulfilment of the quality management requirements ensured the technical competence of the laboratory. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of element measurements in relevant matrices. Having an accreditation was not mandatory. However, when applicable the accreditation scope is stated in the list of participants (see Section 1).

Sixteen laboratories participated in the characterisation exercise. Each laboratory received two vials of ERM-CD281 and was requested to provide 6 independent results, 3 per vial. The characterisation samples were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations (if necessary) and measurements had to be spread over two days and reported on dry mass basis. The water content had to be determined in each ERM-CD281 vial three times (Section 6.2).

As a quality control sample, each participant received a sample of BCR-281 Rye Grass as blind sample to perform a single analysis. The results for this sample have been used only to support the evaluation of the characterisation results (to confirm outliers, see Section 6.4), and therefore are not reported here.

6.2 Dry mass determination

For all measurements carried out during ERM-CD281 certification (homogeneity, stability and characterisation studies) the following protocol for dry mass determination was applied:

Dry mass determination should be carried out on a separate portion of at least 1 g, by drying in an oven at $105\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ until constant mass (separate weighings should not differ by more than 5 mg) is attained.

The water content determined by the laboratories was in the range of 2 wt. % to 6 wt. %. However, results within each laboratory and over a longer time (up to one year) were consistent.

6.3 Methods used

Variety of acid digestion methods with different quantification steps (ICP-OES, ICP-QMS, ICP-SFMS, AAS, AFS) as well as methods without sample preparation (NAA, DMA) were used to characterise the material. Quantification was based on different principles: atomic emission, mass spectrometry, atomic absorption as well as neutron capture. It is rather unlikely that all these methods should be biased in the same way.

All methods used during the characterisation study are summarised in Annex F. The lab-method code consists of a number assigned to each laboratory (e.g. L01) and abbreviation of the measurement method used, (e.g. ICP-SFMS). Symbols 'a' and 'b' distinguish between measurements performed in one laboratory with different sample preparation and/or with different instrumentation, e.g. L01a ICP-SFMS and L01b ICP-SFMS.

6.4 Evaluation of results

The characterisation campaign resulted in 10 to 14 datasets per element. All individual results of the participants, grouped per element are displayed in tabular and/or graphical form in Annex G.

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the analysis protocol: sample preparations and measurements performed on two days, analysis order and water content determination.
- correctness of the measurements based on common knowledge,
- measurement RSD for single dataset: acceptance value was 10 % and less (as obtained for the homogeneity measurements),
- absence of 'less than' and negative values,
- method performance, i.e. delivery of incorrect results for more than half of the analysed elements within one quantification method clearly indicates that the method is not under control. This was verified with the QC sample.

Based on the above some datasets were rejected as not technically valid (see Table 6).

Table 6: Datasets that showed non-compliances with the analysis protocol and technical specifications, and action taken

| Element | Lab-method code | Description of problem | Action taken |
|----------------|-----------------|--|---|
| Se | L01 AFS | RSD about 30 % | Results rejected as not technically valid |
| Pb | L01 ICP-OES | Lab reported 'less than' values | |
| Sn | L02 ICP-OES | Lab reported doubts about the results and negative value. | |
| As, Sb, Se | L02 AFS | Lab reported doubts about the results for Se and Sb. RSD about 40 % for As and 85 % (Sb and Se). | |
| Sn | L03 ICP-SFMS | RSD about 15 % | |
| Cr, Mn, Sb, Zn | L04 NAA | Samples were prepared the same day. Additionally, Mn was measured on one day. Cr, Sb and Zn were measured on three different days however each vial (3 subsamples) was analysed within one day (1 st day: vial 1; 2 nd day: vial 2 and 3 rd day: QC samples). Mn was determined on one day (6 subsamples + QC sample). However, there was no significant difference among the results for ERM samples within and between days, and the results for QC samples were correct. Moreover, sample irradiation requires 10 days up to 1 month depending on the element. | Results accepted |

Table 6: (continued)

| Element | Lab-method code | Description of problem | Action taken |
|---|-------------------------|--|---|
| Se | L06 ICP-QMS | Lab reported unexpected problems caused by the DRC technology. | Results rejected as not technically valid |
| Se | L06 ICP-SFMS | RSD about 12 % | |
| As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Zn | L07 ICP-QMS | Lab reported 'less than' values for As, Hg and Sb. For 6 out of 9 remaining elements, RSD was above 10 % (B, Cd, Mn, Ni, Pb and Zn). Additionally, QC results differed from the reference value by 17 % – 87 % (B, Cd, Cr, Cu, Ni and Zn). | Results rejected as not technically valid |
| As, Cd, Cu, Hg, Ni, Se, Sn | L07 k ₀ -NAA | Lab reported 'less than' values. | |
| Se, Sn | L07 ET-AAS | Lab reported 'less than' values for Se. RSD for Sn about 40 % | |
| Cd, Cu, Ni, Pb, Zn | L08 ID ICP-QMS | Samples were prepared the same day but in two independent microwave runs, and additionally in the sequence as requested in the analysis protocol. | Results were accepted |
| Se | L08 ID ICP-SFMS | RSD about 17 % | Results rejected as not technically valid |
| As, Sb | L10 HG-AFS | Measurements below LOQ and with RSD about 30 %. | |
| B, Se | L10 ET-AAS | Measurements of B below LOQ with RSD about 55 %. RSD for Se about 14 % | |
| Hg | L10 CV-AAS | RSD about 30 % | |
| Hg | L11 CV-AAS | The sample weighing was performed the same day. However, the digestions and measurements were carried out on separated days. | Results were accepted |
| As, Se, Sn | L12 ICP-QMS | RSD for As above 15 %. For QC sample lab reported 'less than' values for Se and Sn, and for As significantly higher value. | Results rejected as not technically valid |
| As, Sn | L13 ICP-QMS | RSD about 30 % (As) and 50 % (Sn) | |
| Sn | L16 ID ICP-SFMS | Measurements performed under repeatability conditions. However, sample preparations (the largest source of result variations in IDMS analysis) were performed on two days. Water content was determined twice. However, the results within a vial were consistent. | Results were accepted |

Further, the technically valid data were subjected to outlier tests (Dixon, Nalimov, Grubbs, Cochran). Based on these tests and visual inspection some outliers could be identified. No data was excluded from the evaluation based on outlier tests alone. The findings were

verified by the QC sample. The data sets that were found to be outliers are listed, together with the action taken in Table 7.

Table 7: Results of the statistical evaluation of technically valid datasets

| Element | Lab-method code | Description of problem | Action taken |
|----------------------------|-----------------|---|-----------------------|
| Sb | L01a ICP-SFMS | Results were identified as outlier by all tests except Cochran test. However, measurement uncertainty was comparable to and overlapped with uncertainties from other labs. | Results were accepted |
| As | L14 ICP-QMS | Results were identified as outlier by all tests except Dixon test. Additionally, the QC sample value deviated significantly from the certified value. | Results were rejected |
| Cd, Mo, Pb, Sn | L10 ET-AAS | Results were identified as outlier by all tests for Cd, Pb, Sn and by three tests for Mo. Additionally, the QC sample values deviated significantly from the certified value or results of other labs (Sn). Moreover, the other elements measured with AAS were rejected after the technical evaluation (see Table 6). | Results were rejected |
| Cd, Cr, Cu, Mn, Mo, Pb, Zn | L02 ICP-OES | Labs reported large expanded uncertainties comparing to the uncertainties of the other labs. Both labs applied similar approach to assess the uncertainties: 2 x reproducibility standard deviation (from method validation/quality control charts/interlaboratory comparisons). It could be assumed that the uncertainty is overestimated. | Results were accepted |
| Cr, Cu, Mn, Mo, Ni, Zn | L05 ICP-QMS | | |

The certified value was calculated as the mean of means of the accepted datasets. The contribution of the material characterisation to the uncertainty of the certified value u_{char} was estimated as the standard error of the mean of means, and was calculated as the relative standard deviation divided by the square root of accepted datasets. The resulting data are summarised in Table 8.

Table 8: Summary of the characterisation study

| Element | Number of independent, valid datasets | Mean of laboratory means ^a [mg/kg] | $u_{\text{char, rel}}$ [%] |
|---------|--|--|----------------------------|
| As | 7 | 0.0419 | 3.9 |
| B | 7 | 5.50 | 3.4 |
| Cd | 7 | 0.1199 | 1.9 |
| Cr | 12 | 24.77 | 2.3 |
| Cu | 10 | 10.15 | 1.7 |
| Hg | 9 | 0.01635 | 5.1 |
| Mn | 12 | 81.6 | 1.7 |
| Mo | 9 | 2.219 | 1.8 |
| Ni | 11 | 15.22 | 1.5 |
| Pb | 8 | 1.669 | 1.9 |
| Sb | 7 | 0.0423 | 3.0 |
| Se | 6 | 0.0225 | 3.5 |
| Sn | 6 | 0.0619 | 4.3 |
| Zn | 13 | 30.47 | 1.4 |

^a: reported on dry mass basis (see Section 6.2)

7 Assigned values

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 8 was assigned as a certified value for the elements.

The certified uncertainty consists of uncertainties related to characterisation, u_{char} (see Section 6.4), between-bottle heterogeneity, u_{bb} (see Section 4.1) and degradation during long-term storage, u_{tls} (see Section 5.2). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{\text{CRM, rel}}$) as given by:

$$U_{\text{CRM, rel}} = k \cdot \sqrt{u_{\text{char, rel}}^2 + u_{\text{bb, rel}}^2 + u_{\text{tls, rel}}^2} \quad (6)$$

where:

k : coverage factor equalling 2, representing a level of confidence of about 95 %.

The certified values and their uncertainties are summarised in Table 9.

Table 9: Certified values and their uncertainties for ERM-CD281

| Element | Certified value ^a [mg/kg] | $u_{\text{char, rel}}$ [%] | $u_{\text{bb, rel}}$ [%] | $u_{\text{tls, rel}}$ [%] | $U_{\text{CRM, rel}}$ [%] | U_{CRM} [mg/kg] |
|---------|---|-------------------------------|-----------------------------|------------------------------|------------------------------|-----------------------------|
| As | 0.042 | 3.9 | 9.4 | 5.4 | 23.0 | 0.010 |
| B | 5.5 | 3.4 | 0.8 | 1.5 | 7.6 | 0.5 |
| Cd | 0.120 | 1.9 | 0.8 | 1.9 | 5.6 | 0.007 |
| Cr | 24.8 | 2.3 | 0.6 | 0.9 | 5.1 | 1.3 |
| Cu | 10.2 | 1.7 | 0.6 | 1.2 | 4.3 | 0.5 |
| Hg | 0.0164 | 5.1 | 3.3 | 2.8 | 13.4 | 0.0022 |
| Mn | 82 | 1.7 | 0.5 | 1.2 | 4.3 | 4 |
| Mo | 2.22 | 1.8 | 1.4 | 1.3 | 5.2 | 0.12 |
| Ni | 15.2 | 1.5 | 0.7 | 1.0 | 3.9 | 0.6 |
| Pb | 1.67 | 1.9 | 2.3 | 1.2 | 6.4 | 0.11 |
| Sb | 0.042 | 3.0 | 1.5 | 7.2 | 15.9 | 0.007 |
| Se | 0.023 | 3.5 | 3.4 | 4.8 | 13.7 | 0.004 |
| Sn | 0.062 | 4.3 | 2.9 | 6.4 | 16.5 | 0.011 |
| Zn | 30.5 | 1.4 | 0.3 | 1.1 | 3.6 | 1.1 |

^a: reported on dry mass basis (see Section 6.2)

7.2 Additional material information

The results of semi-quantitative screening analysis using ICP-SFMS is given as additional material information (see Table 10). The elements were determined using 18 scans over the mass range, resulting in a total measurement time of 300 s. The results are an average of triplicate measurements.

Table 10: Additional material information

| Element | Mass fraction ^a [g/kg] |
|---------|-----------------------------------|
| Ca | 6.3 |
| Fe | 0.18 |
| K | 34 |
| Mg | 1.6 |
| Na | 4.0 |
| P | 2.8 |
| S | 3.4 |
| Si | 1.3 |

^a: average of triplicate measurements reported on dry mass basis

8 Metrological traceability and commutability

8.1 Metrological traceability

Traceability of the certified values to the International System of Units (SI) is ensured through the set-up of the characterisation. The participating laboratories used a number of different methods for the sample preparation as well as for the final determination, thus eliminating any possibility of method dependent results. Only validated methods were used. Different calibrants were employed, including commercial standard solutions and CRMs. Most of the laboratories also used matrix CRMs for quality control (see Annex F). The values of the calibrants and QC samples are traceable to the SI, as stated on the respective certificates. In addition, the agreement between the results confirms absence of any significant method bias and demonstrates the identity of the analytes.

8.2 Commutability

Commutable CRMs should exhibit a similar analytical behaviour for given methods as a real laboratory sample. The laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding sample preparation, calibration and detection. The good agreement between the results obtained indicates commutability of the material. However, it has to be kept in mind that the certified reference materials might show behaviour different from that of real samples, in particular during digestion, due to their small particle sizes in contrast to the possibility larger particle sizes encountered for real laboratory samples, and the intensive processing that these materials have undergone.

9 Instructions for use

9.1 Storage conditions

The materials shall be stored at $18\text{ °C} \pm 5\text{ °C}$ and in the dark. Care shall be taken to avoid moisture pickup once the vials are open, as the material is hygroscopic. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.2 Safety and protection for the environment

The usual laboratory safety measures apply.

9.3 Use of the material

The vials shall be shaken by turning upside down for at least 2 min before opening to ensure the material re-homogenisation.

9.4 Minimum sample intake

The minimum sample intake representative for all elements is 200 mg. However, lower sample intakes can be also applied, i.e. 100 mg for all elements As, B, Cr, Hg, Mn, Mo, Ni, Pb, Se, Sn and Zn and 50 mg for As, Cr, Hg, Pb and Sn.

9.5 Dry mass correction

Dry mass determination shall be carried out on a separate portion of at least 1 g, by drying in an oven at $105\text{ °C} \pm 2\text{ °C}$ until constant mass (separate weighings should not differ by more than 5 mg) is attained. Weighing of the samples for dry mass determination and weighing for the analysis shall be done at the same time to avoid differences due to possible take up of moisture by the material.

9.6 Use of the certified value

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [9]).

Use as a calibrant

It is not recommended to use this matrix material as calibrant. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

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8. T.P.J. Linsinger, J. Pauwels, A. Lamberty, H.G. Schimmel, A. M. H. van der Veen and L. Siekmann, 2001, *Fresenius J. Anal. Chem.*, 370, 183-188.
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Acknowledgments

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Work of the processing team (IRMM) is appreciated.

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Annexes

Annex A: Results of the homogeneity measurements

ERM-CD281, B: mass fractions reported on dry mass basis [mg/kg]

| Vial # | Replicate 1 | Replicate 2 | Replicate 3 |
|--------|-------------|-------------|-------------------|
| 2 | 5.41 | 5.49 | 5.47 |
| 172 | 5.55 | 5.36 | 5.52 |
| 301 | 5.41 | 5.48 | 5.48 |
| 458 | 5.55 | 5.66 | 5.68 |
| 636 | 5.52 | 5.51 | 5.80 |
| 749 | 5.60 | 5.37 | 5.18 ^a |
| 900 | 5.50 | 5.80 | 5.46 |
| 1027 | 5.61 | 5.75 | 5.39 |
| 1190 | 5.46 | 5.75 | 5.09 ^a |
| 1364 | 5.40 | 5.64 | 5.72 |
| 1519 | 5.39 | 5.46 | 5.45 |
| 1714 | 5.49 | 5.73 | 5.51 |
| 1940 | 5.51 | 5.78 | 5.59 |
| 2146 | 5.74 | 5.79 | 5.54 |
| 2385 | 5.58 | 5.60 | 5.54 |

^a: Outlier on a 95 % confidence level

ERM-CD281, Cd: mass fractions reported on dry mass basis [mg/kg]

| Vial # | Replicate 1 | Replicate 2 | Replicate 3 |
|--------|-------------|-------------|-------------|
| 2 | 0.133 | 0.131 | 0.126 |
| 172 | 0.130 | 0.129 | 0.127 |
| 301 | 0.135 | 0.130 | 0.126 |
| 458 | 0.130 | 0.126 | 0.122 |
| 636 | 0.127 | 0.129 | 0.121 |
| 749 | 0.132 | 0.130 | 0.127 |
| 900 | 0.126 | 0.130 | 0.136 |
| 1027 | 0.130 | 0.129 | 0.129 |
| 1190 | 0.132 | 0.131 | 0.128 |
| 1364 | 0.131 | 0.130 | 0.124 |
| 1519 | 0.127 | 0.130 | 0.125 |
| 1714 | 0.136 | 0.133 | 0.123 |
| 1940 | 0.129 | 0.131 | 0.123 |
| 2146 | 0.130 | 0.131 | 0.125 |
| 2385 | 0.133 | 0.130 | 0.127 |

Annex B: Results of the minimum sample intake measurements

ERM-CD281, As: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|--------|
| 1 | 0.0354 | 0.0465 | 0.0272 |
| 2 | 0.0347 | 0.0361 | 0.0284 |
| 3 | 0.0329 | 0.0324 | 0.0301 |
| 4 | 0.0347 | 0.0308 | 0.0359 |
| 5 | 0.0474 | 0.0279 | 0.0258 |
| 6 | 0.0334 | 0.0336 | 0.0346 |

ERM-CD281, B: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 4.35 | 4.26 | 4.07 |
| 2 | 4.22 | 4.27 | 4.00 |
| 3 | 4.32 | 4.12 | 4.17 |
| 4 | 4.45 | 4.43 | 3.85 |
| 5 | 4.39 | 4.44 | 4.42 |
| 6 | 4.42 | 4.31 | 3.90 |

ERM-CD281, Cd: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 0.122 | 0.118 | 0.119 |
| 2 | 0.122 | 0.121 | 0.107 |
| 3 | 0.120 | 0.118 | 0.108 |
| 4 | 0.121 | 0.112 | 0.122 |
| 5 | 0.121 | 0.113 | 0.117 |
| 6 | 0.119 | 0.114 | 0.118 |

ERM-CD281, Cr: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 21.1 | 20.5 | 21.0 |
| 2 | 21.2 | 20.5 | 20.8 |
| 3 | 21.0 | 20.6 | 21.0 |
| 4 | 20.9 | 20.5 | 20.7 |
| 5 | 20.8 | 20.7 | 20.9 |
| 6 | 21.1 | 20.7 | 20.3 |

ERM-CD281, Cu: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|-------------------|-------|
| 1 | 11.9 | 12.6 ^a | 12.3 |
| 2 | 11.7 | 11.9 | 11.8 |
| 3 | 11.8 | 11.8 | 12.4 |
| 4 | 11.9 | 11.8 | 12.0 |
| 5 | 11.8 | 11.9 | 12.1 |
| 6 | 12.0 | 11.9 | 11.7 |

^a: Outlier on a 95 % confidence level

ERM-CD281, Hg: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|--------|
| 1 | 0.0128 | 0.0114 | 0.0109 |
| 2 | 0.0128 | 0.0116 | 0.0108 |
| 3 | 0.0130 | 0.0117 | 0.0114 |
| 4 | 0.0135 | 0.0120 | 0.0125 |
| 5 | 0.0136 | 0.0120 | 0.0121 |
| 6 | 0.0130 | 0.0121 | 0.0113 |

ERM-CD281, Mn: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 80.8 | 79.9 | 81.1 |
| 2 | 79.3 | 78.0 | 76.3 |
| 3 | 78.9 | 78.1 | 80.9 |
| 4 | 79.9 | 79.1 | 80.0 |
| 5 | 79.5 | 78.3 | 81.2 |
| 6 | 80.1 | 78.9 | 77.0 |

ERM-CD281, Mo: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 1.98 | 1.91 | 1.93 |
| 2 | 1.99 | 1.93 | 1.84 |
| 3 | 2.00 | 1.93 | 1.89 |
| 4 | 1.98 | 1.93 | 1.92 |
| 5 | 1.96 | 1.92 | 1.90 |
| 6 | 1.97 | 1.94 | 1.85 |

ERM-CD281, Ni: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 14.7 | 14.3 | 14.9 |
| 2 | 14.5 | 14.1 | 14.6 |
| 3 | 14.6 | 14.6 | 14.6 |
| 4 | 14.5 | 14.3 | 14.6 |
| 5 | 14.6 | 14.2 | 14.9 |
| 6 | 14.5 | 14.5 | 14.1 |

ERM-CD281, Pb: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 1.53 | 1.45 | 1.50 |
| 2 | 1.51 | 1.46 | 1.42 |
| 3 | 1.51 | 1.48 | 1.49 |
| 4 | 1.56 | 1.47 | 1.50 |
| 5 | 1.53 | 1.47 | 1.44 |
| 6 | 1.52 | 1.49 | 1.43 |

ERM-CD281, Sb: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|--------|
| 1 | 0.0296 | 0.0309 | 0.0295 |
| 2 | 0.0294 | 0.0266 | 0.0294 |
| 3 | 0.0293 | 0.0278 | 0.0301 |
| 4 | 0.0298 | 0.0292 | 0.0280 |
| 5 | 0.0301 | 0.0272 | 0.0309 |
| 6 | 0.0307 | 0.0286 | 0.0281 |

ERM-CD281, Se: mass fractions reported on dry mass basis [mg/kg]

| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|--------|
| 1 | 0.0259 | 0.0189 | 0.0213 |
| 2 | 0.0193 | 0.0247 | 0.0211 |
| 3 | 0.0227 | 0.0206 | 0.0242 |
| 4 | 0.0211 | 0.0171 | 0.0198 |
| 5 | 0.0240 | 0.0252 | 0.0144 |
| 6 | 0.0237 | 0.0172 | 0.0305 |

ERM-CD281, Sn: mass fractions reported on dry mass basis [mg/kg]

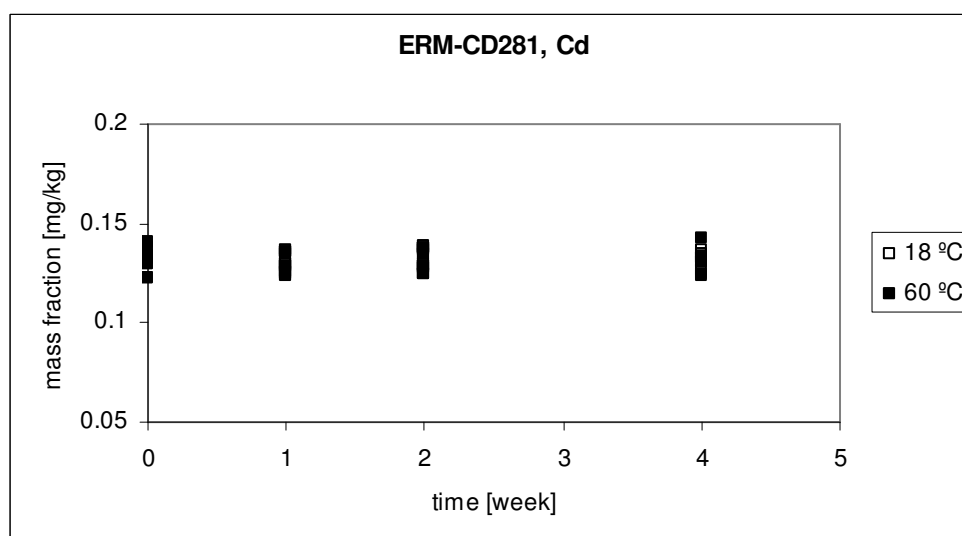
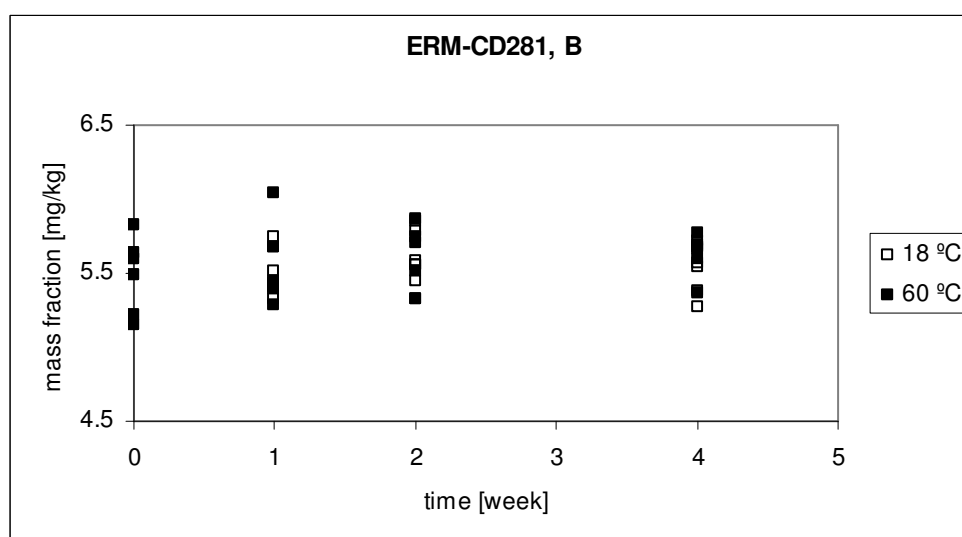
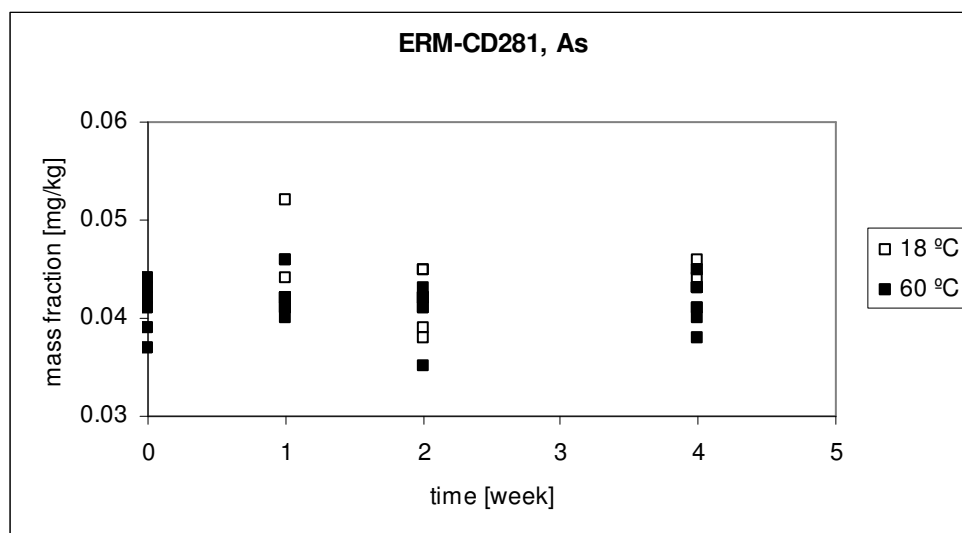
| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|--------|
| 1 | 0.0482 | 0.0494 | 0.0430 |
| 2 | 0.0462 | 0.0393 | 0.0439 |
| 3 | 0.0424 | 0.0511 | 0.0445 |
| 4 | 0.0490 | 0.0441 | 0.0506 |
| 5 | 0.0487 | 0.0475 | 0.0462 |
| 6 | 0.0470 | 0.0464 | 0.0415 |

ERM-CD281, Zn: mass fractions reported on dry mass basis [mg/kg]

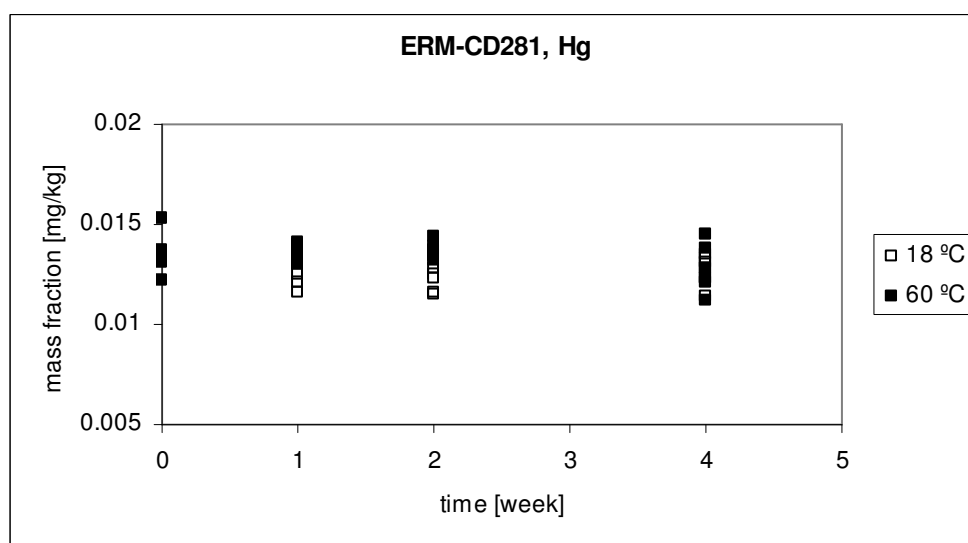
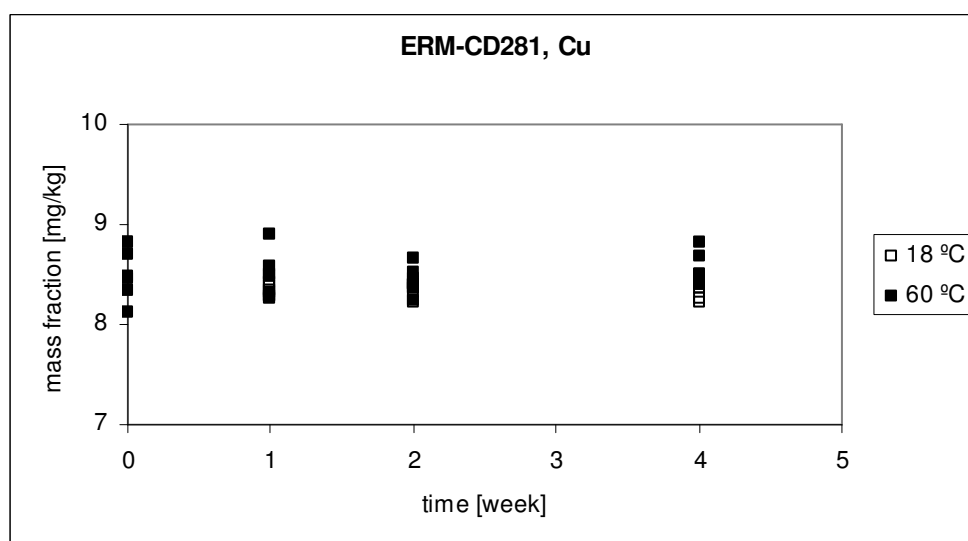
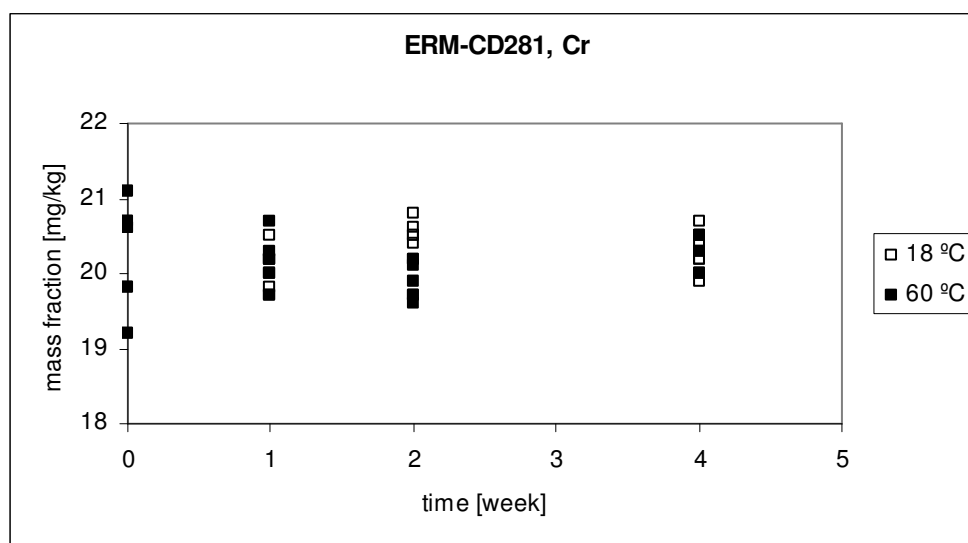
| Replicate # | 200 mg | 100 mg | 50 mg |
|-------------|--------|--------|-------|
| 1 | 27.6 | 26.6 | 26.8 |
| 2 | 27.3 | 26.6 | 25.2 |
| 3 | 27.4 | 26.6 | 26.5 |
| 4 | 27.2 | 27.1 | 26.3 |
| 5 | 27.1 | 26.7 | 26.4 |
| 6 | 27.5 | 26.6 | 25.4 |

Annex C: Results of the short-term stability measurements

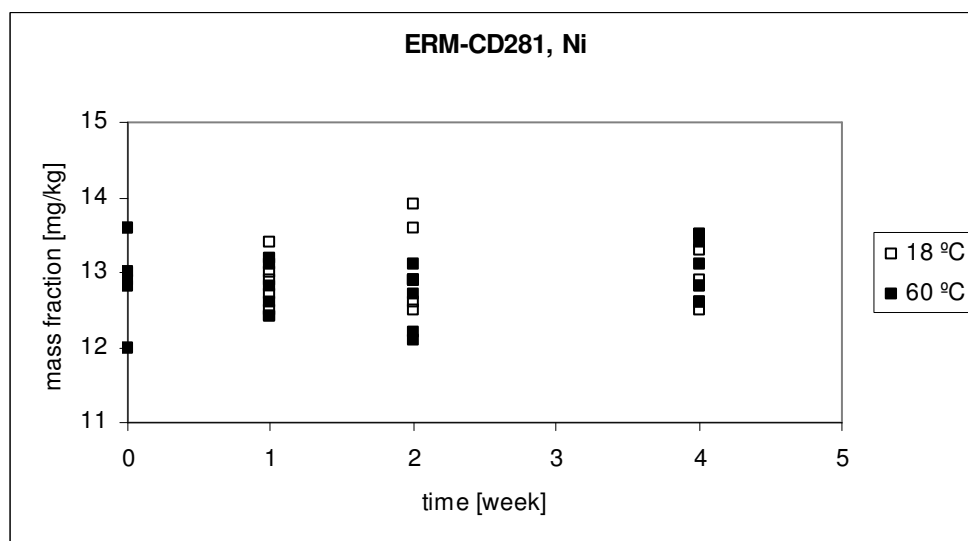
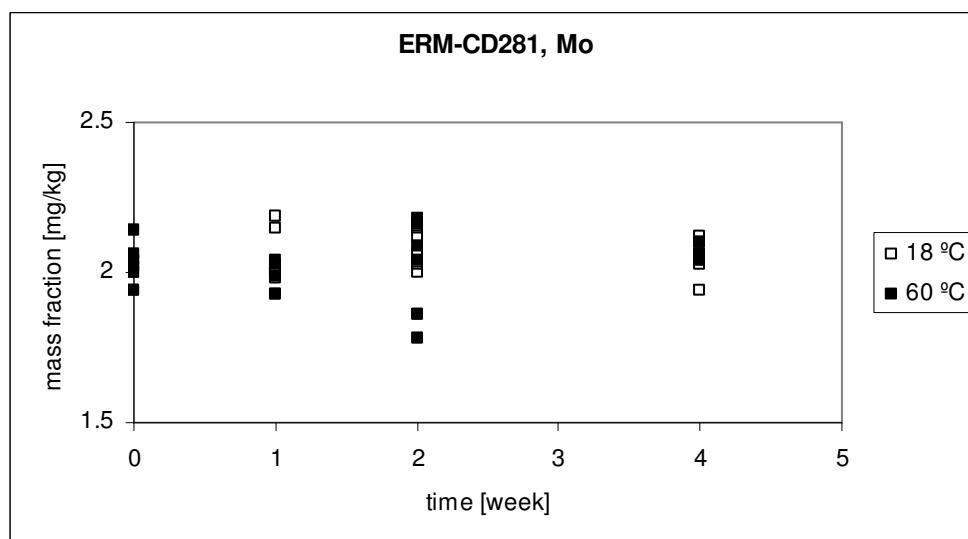
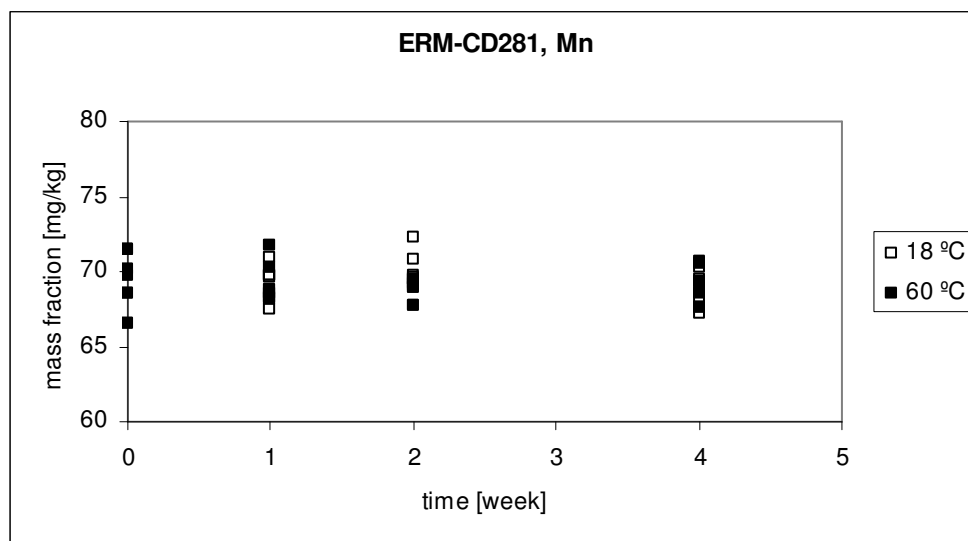
Results reported on dry mass basis



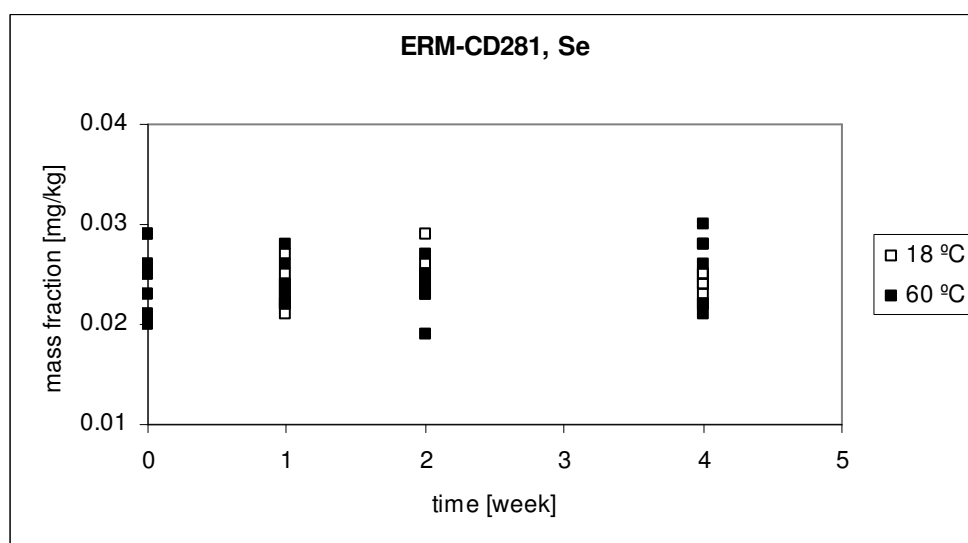
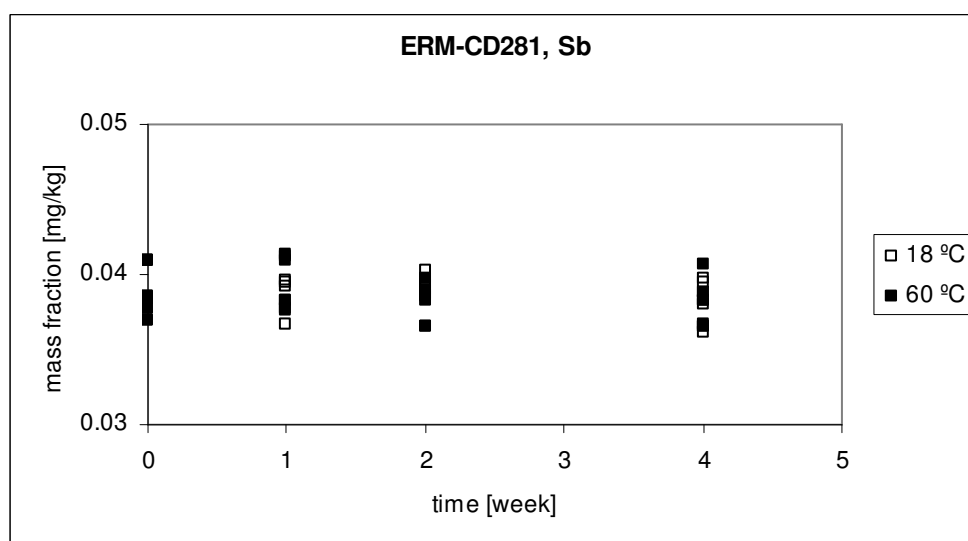
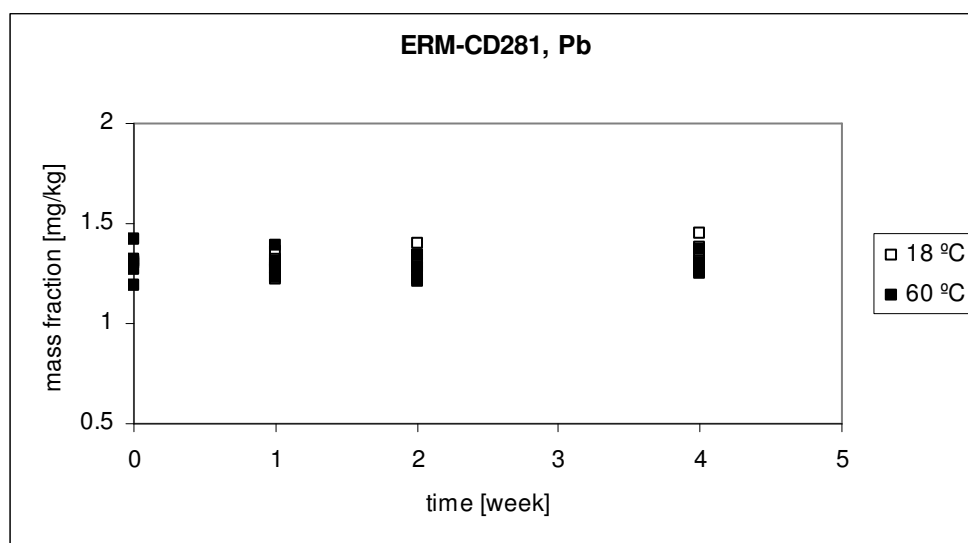
Results reported on dry mass basis



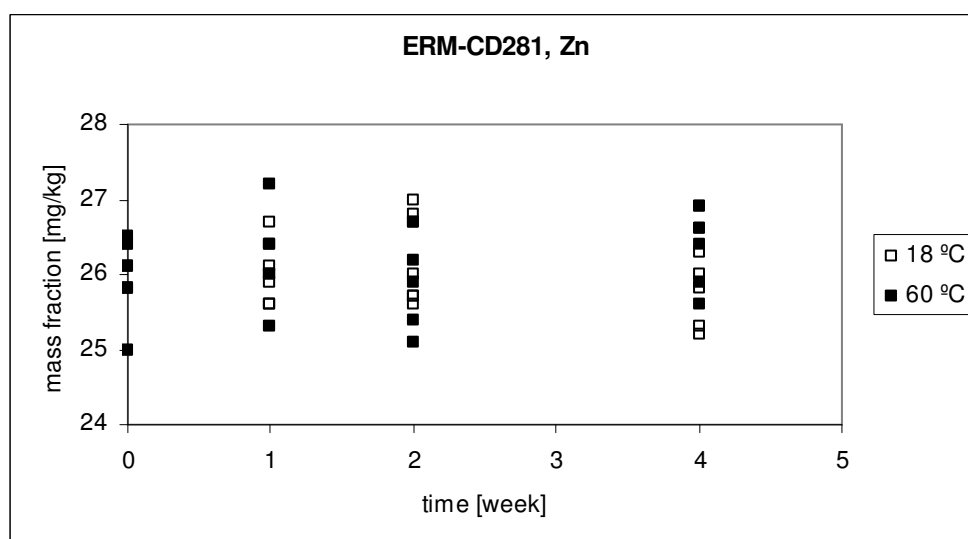
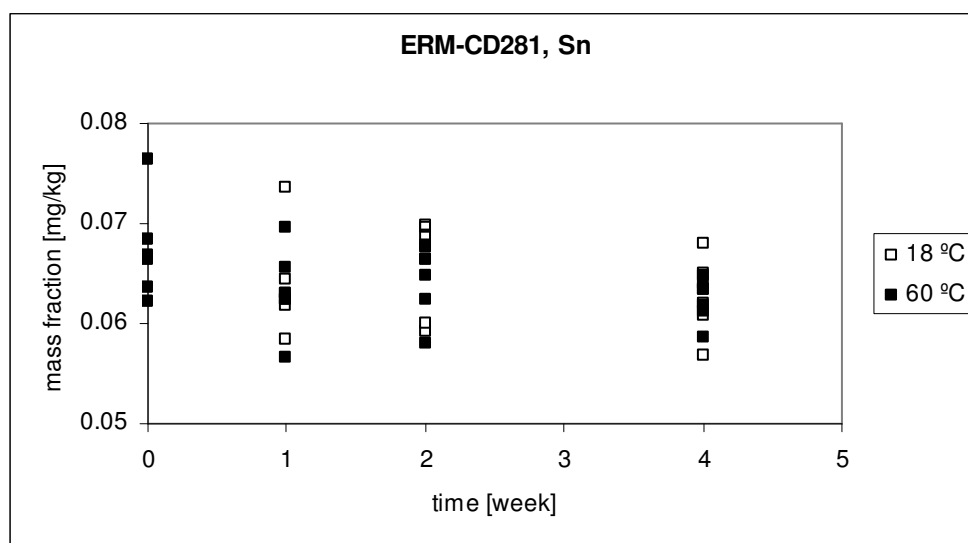
Results reported on dry mass basis



Results reported on dry mass basis

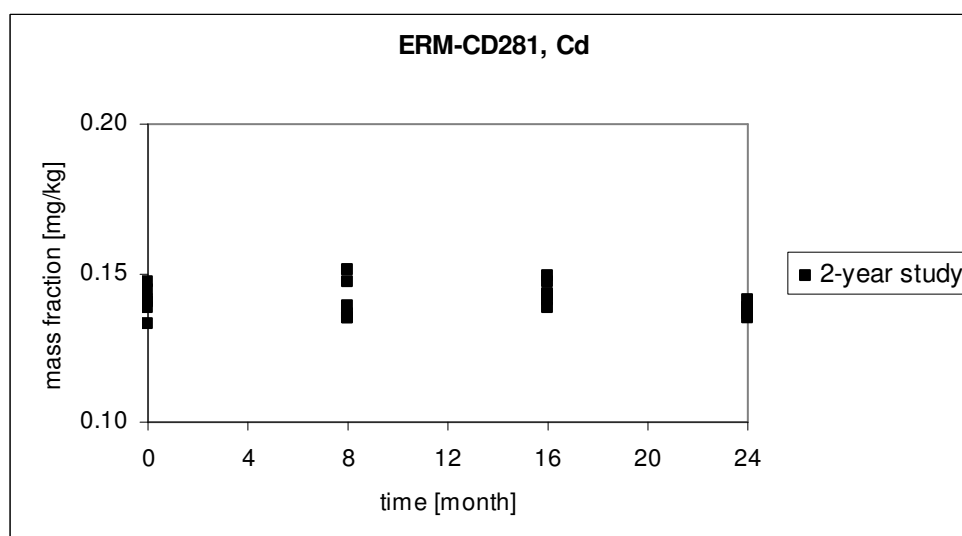
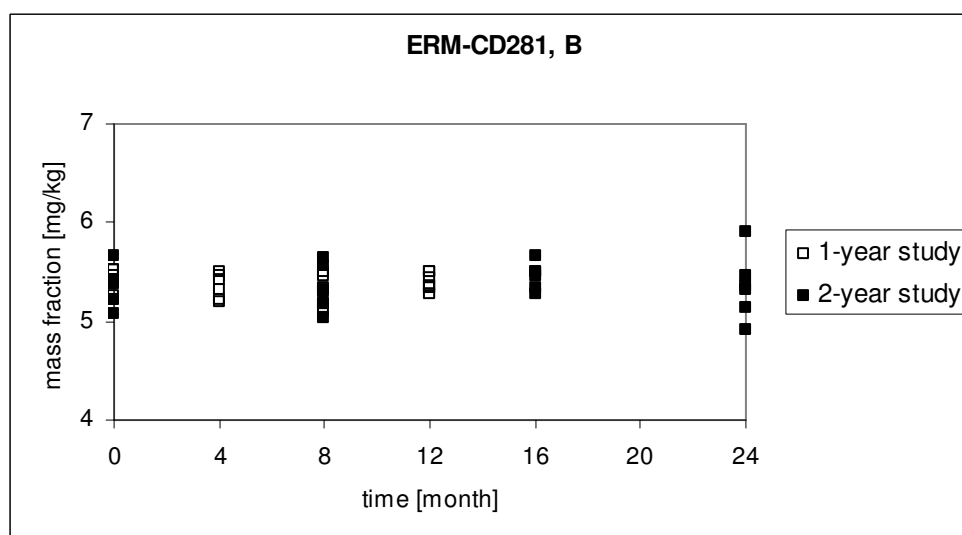
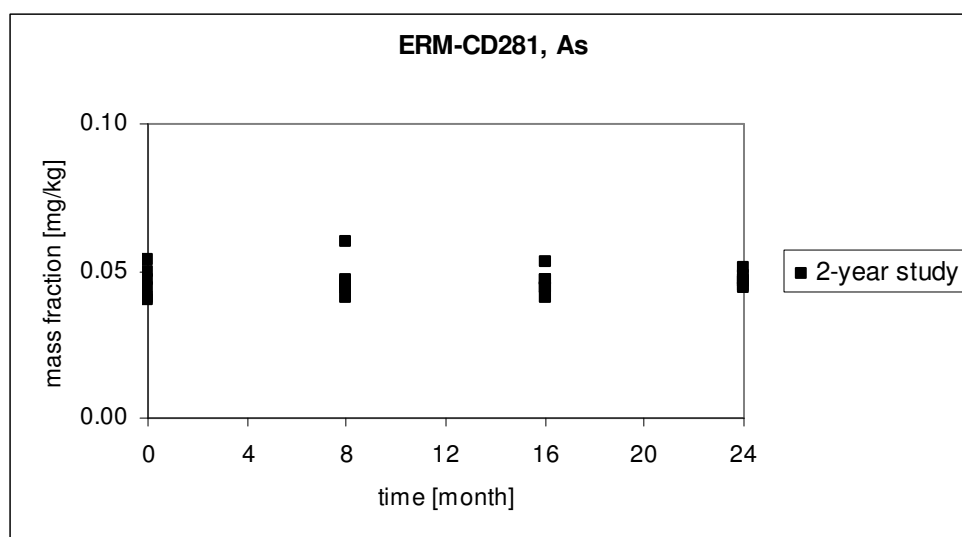


Results reported on dry mass basis

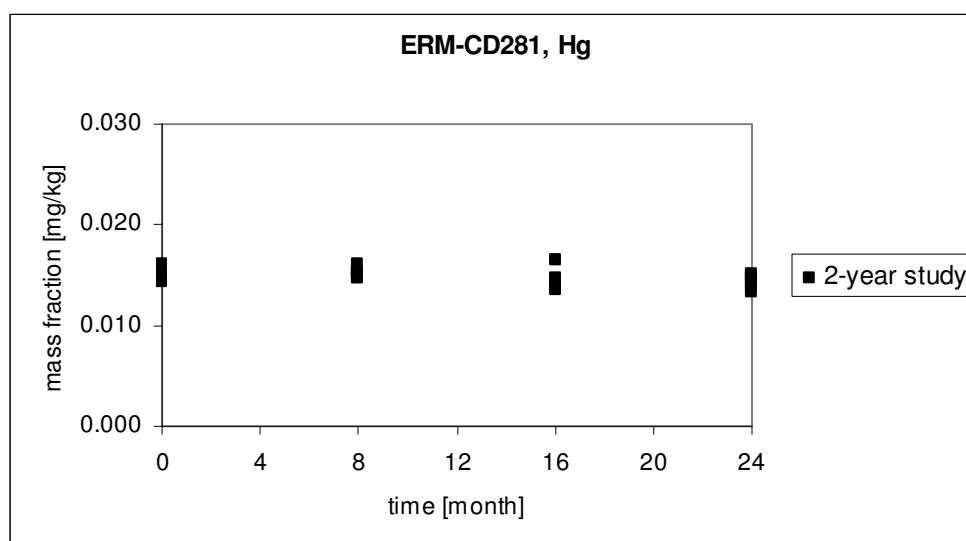
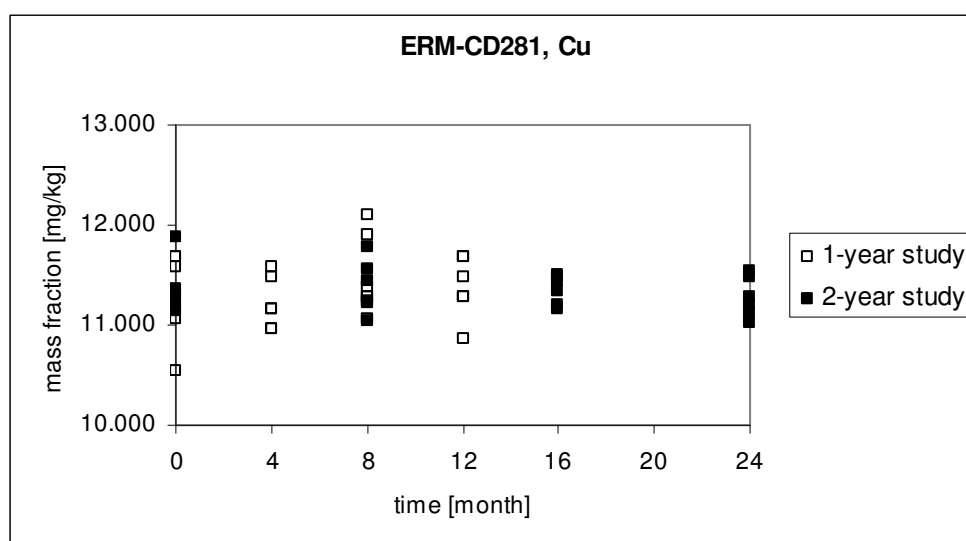
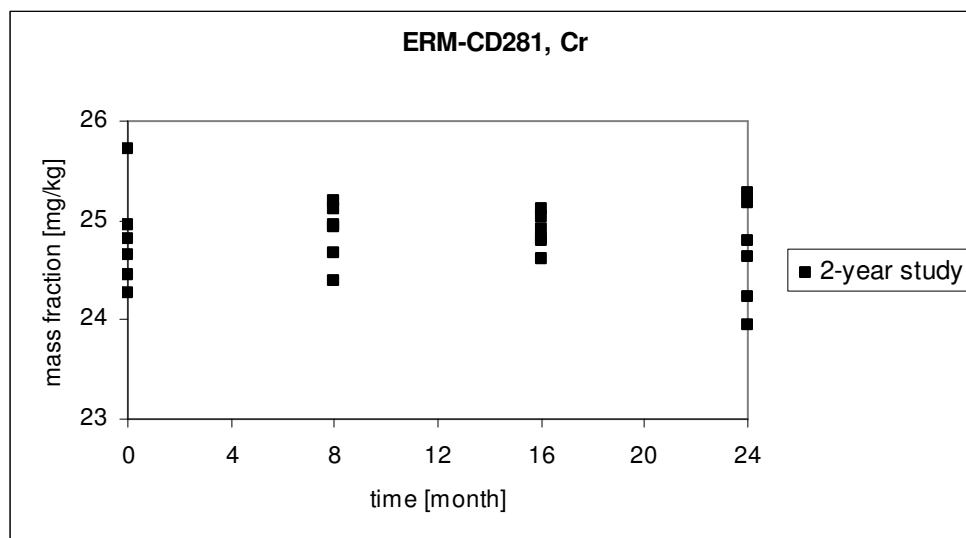


Annex D: Results of the long-term stability measurements

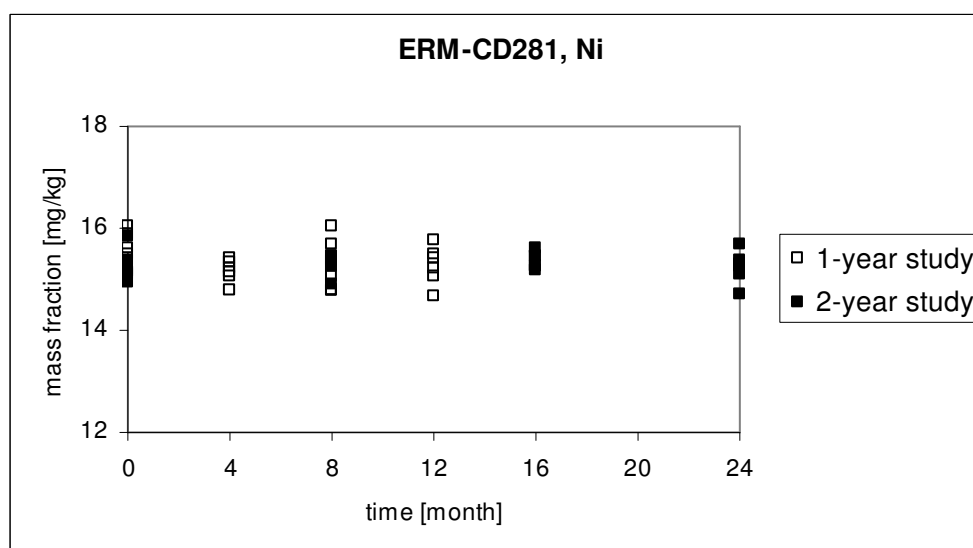
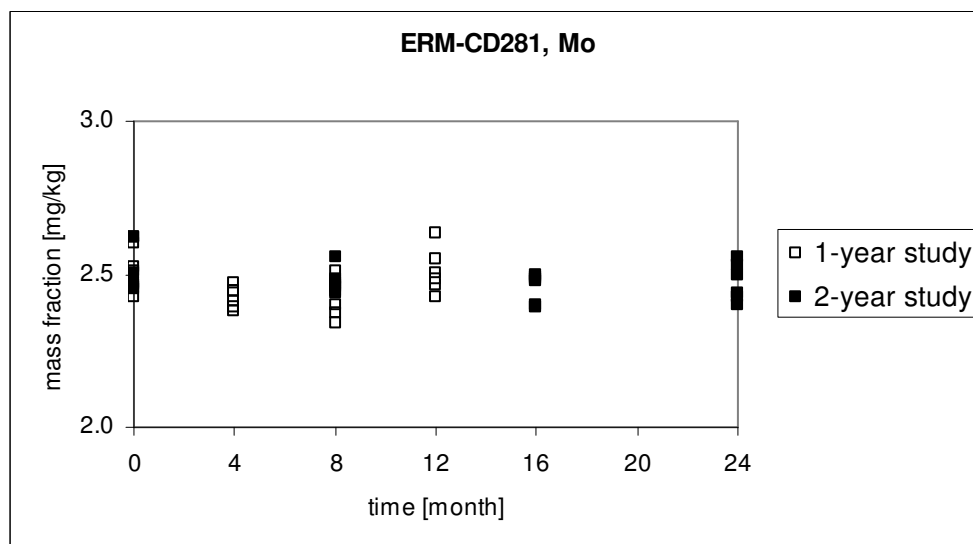
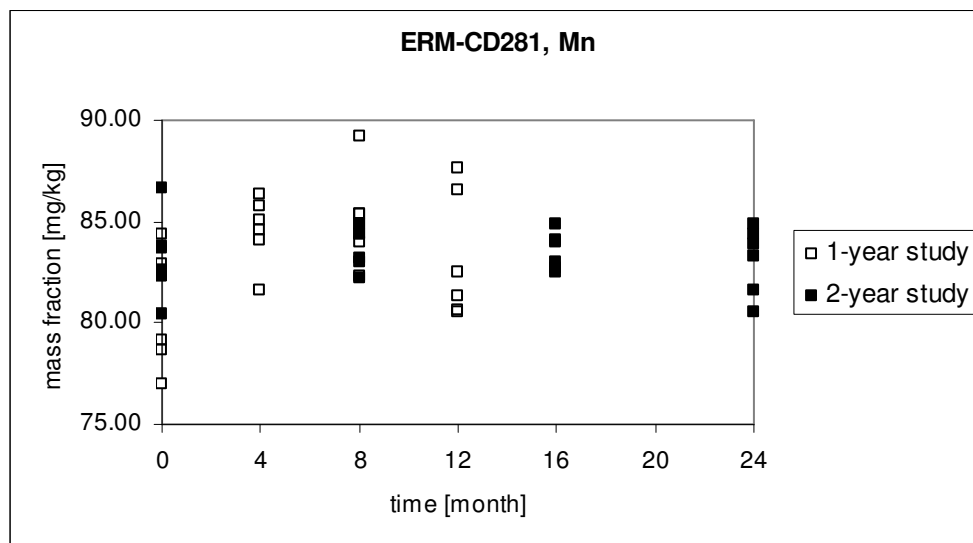
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.



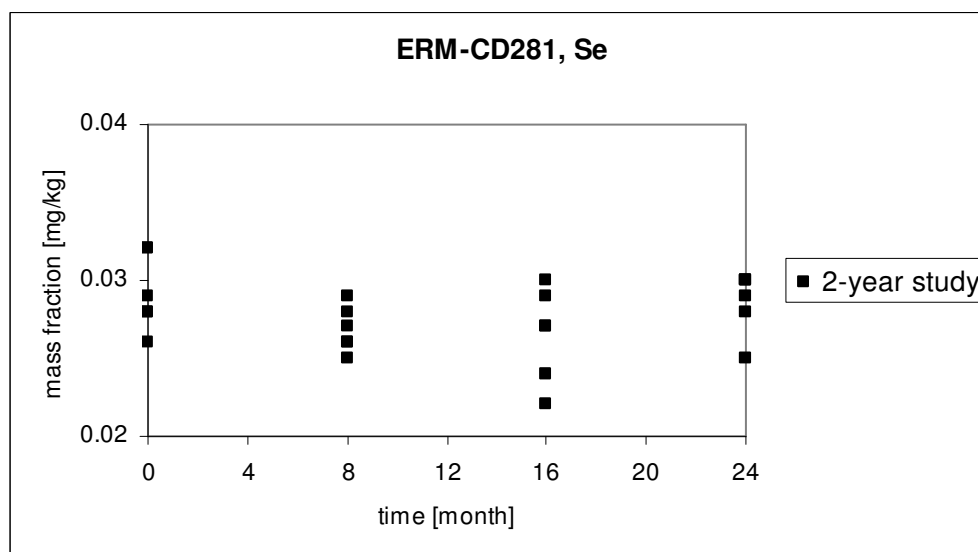
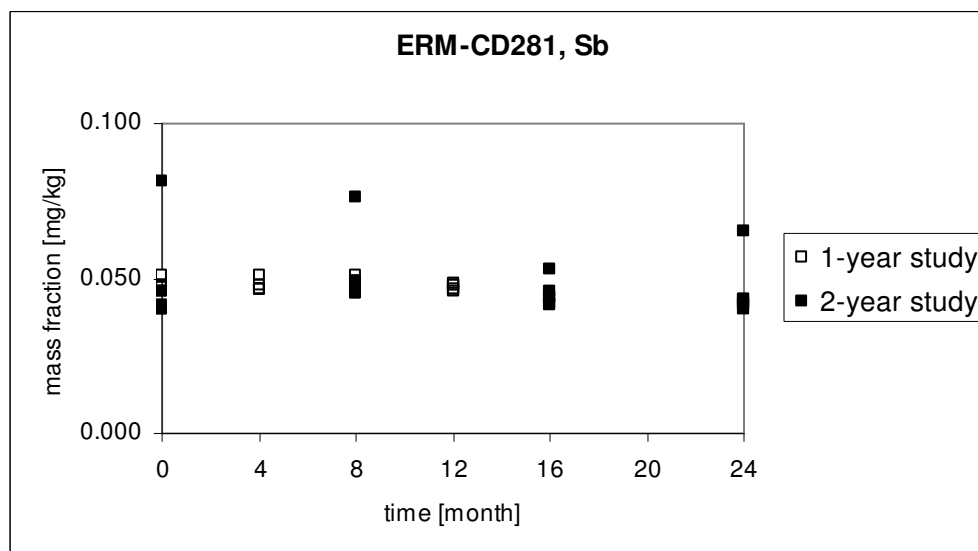
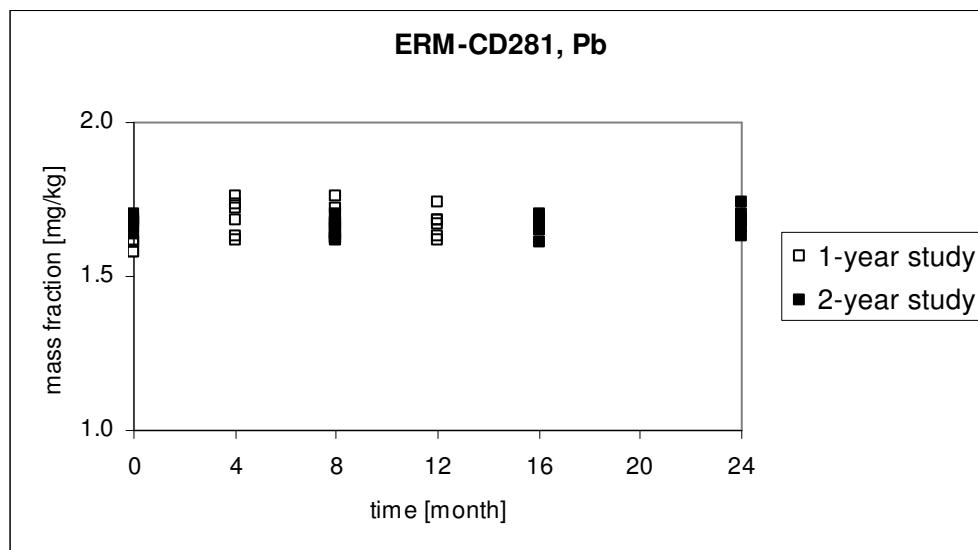
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.



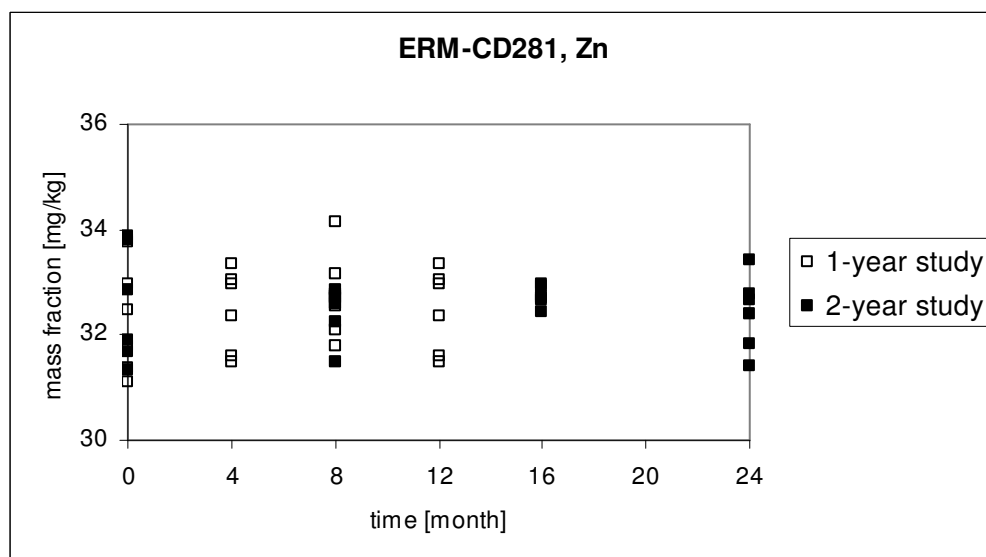
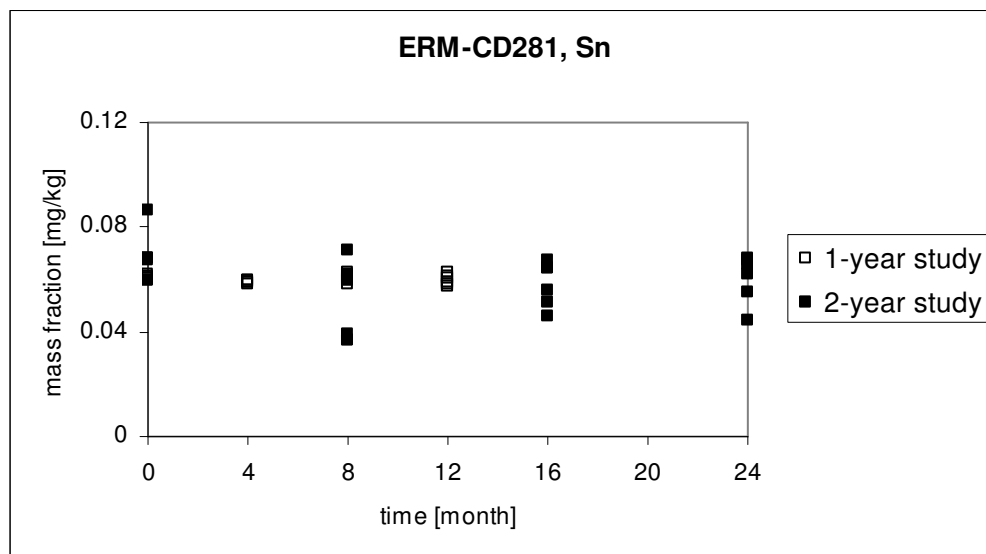
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.



Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

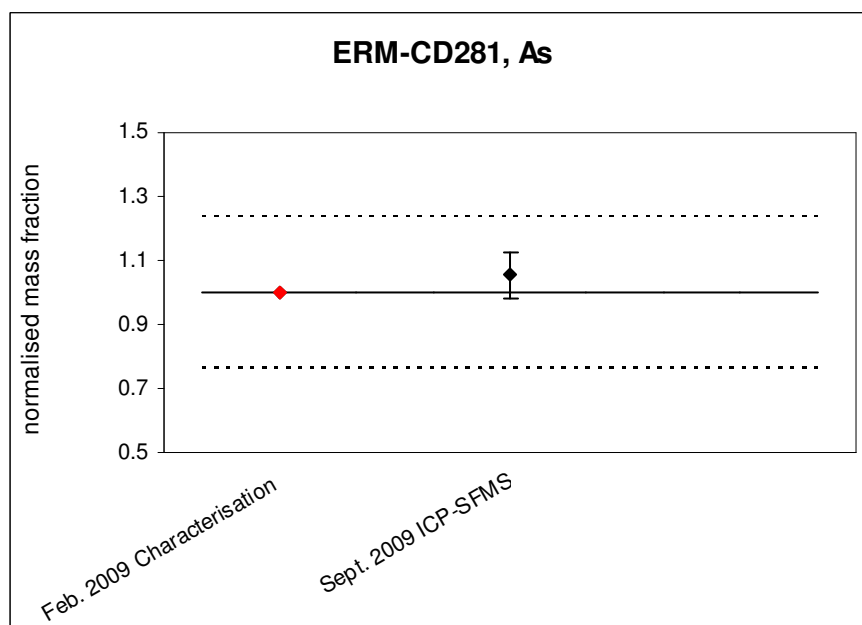
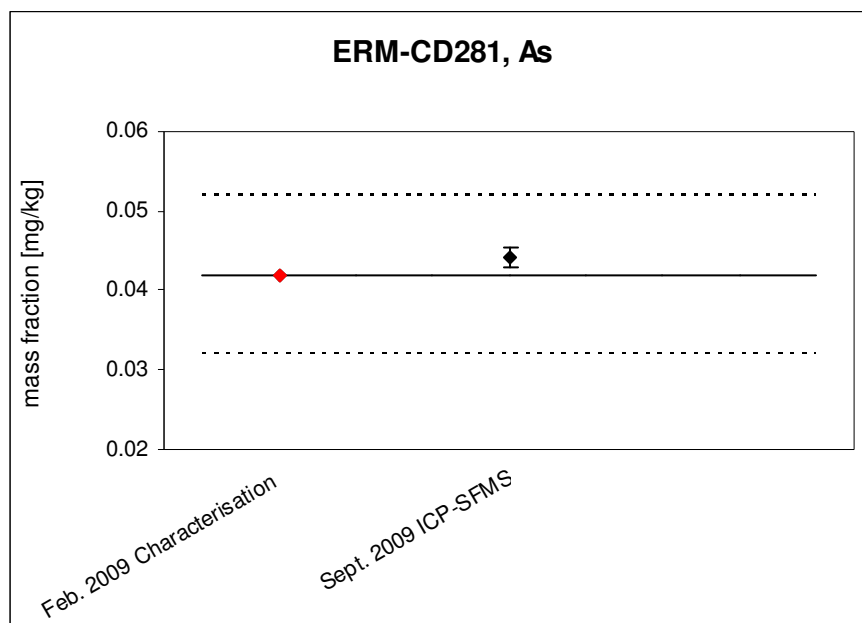


Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

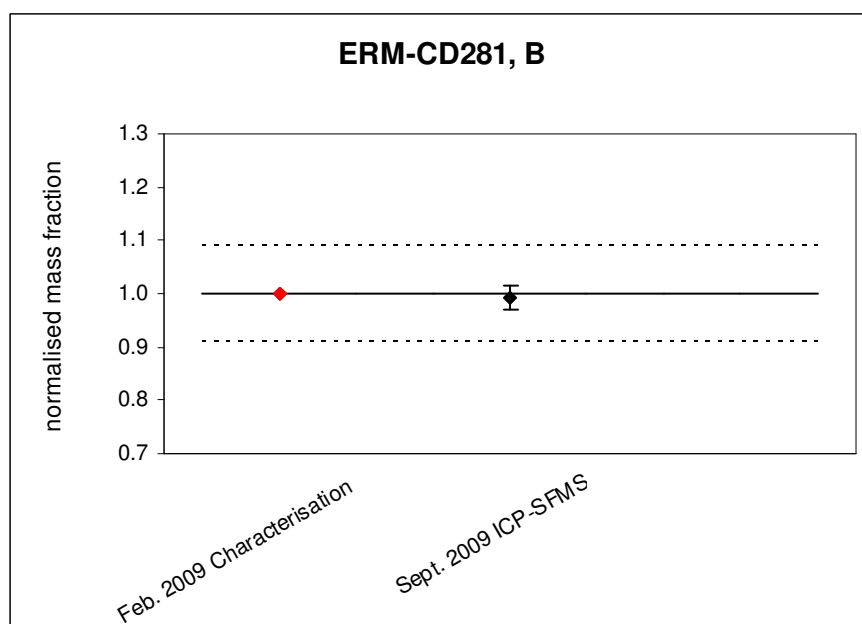
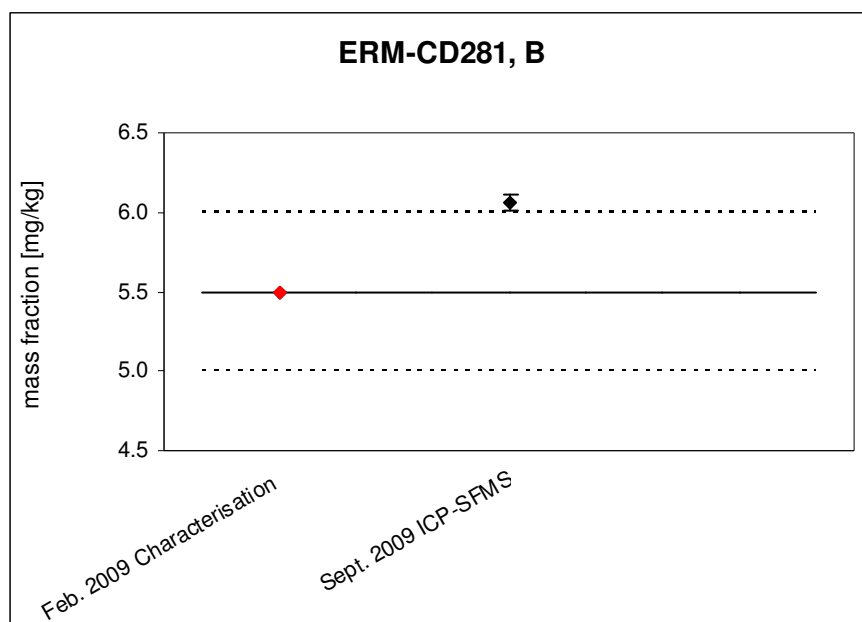


Annex E: Results of the stability control measurements

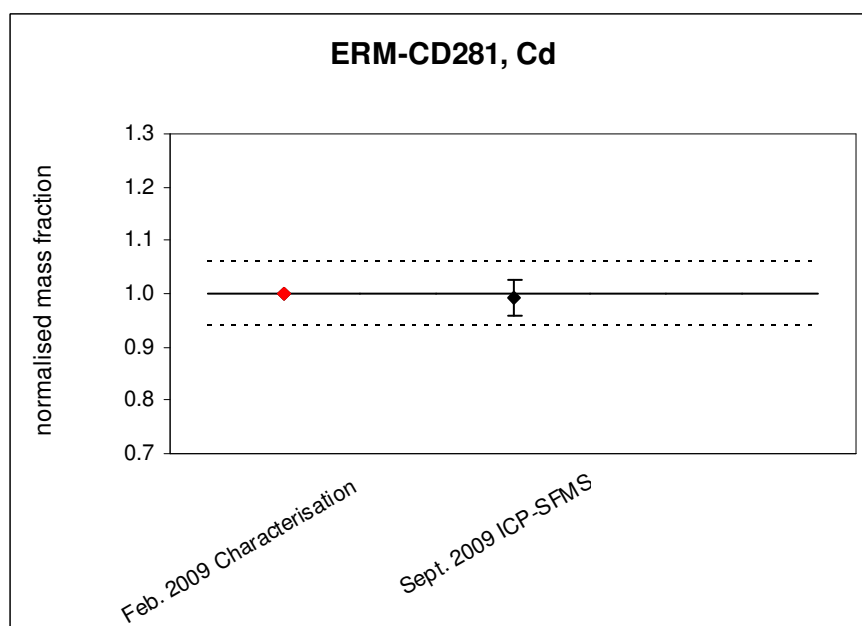
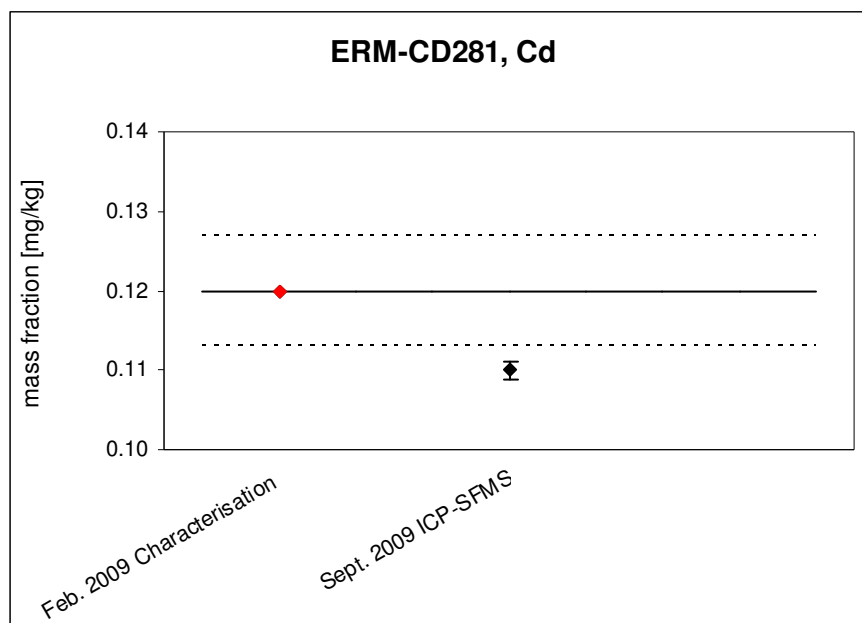
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



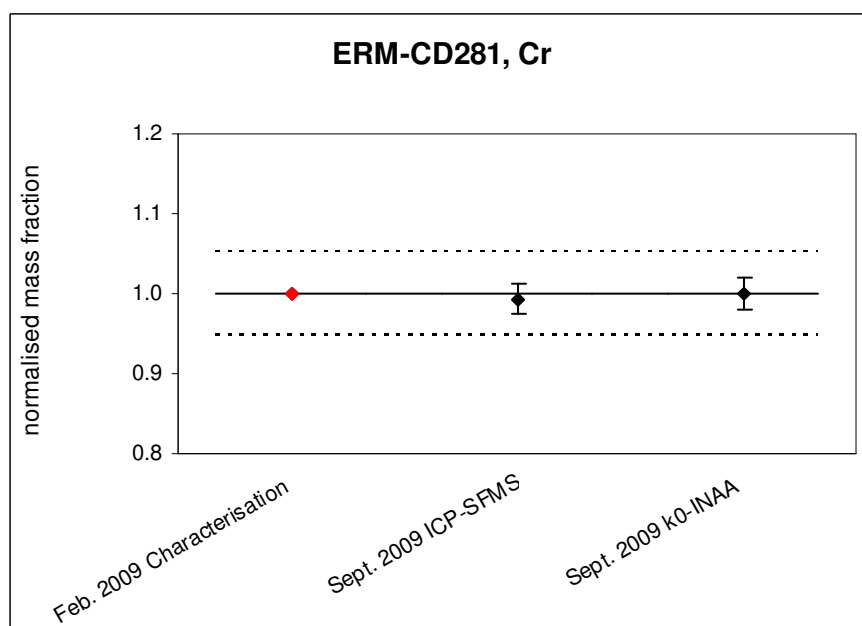
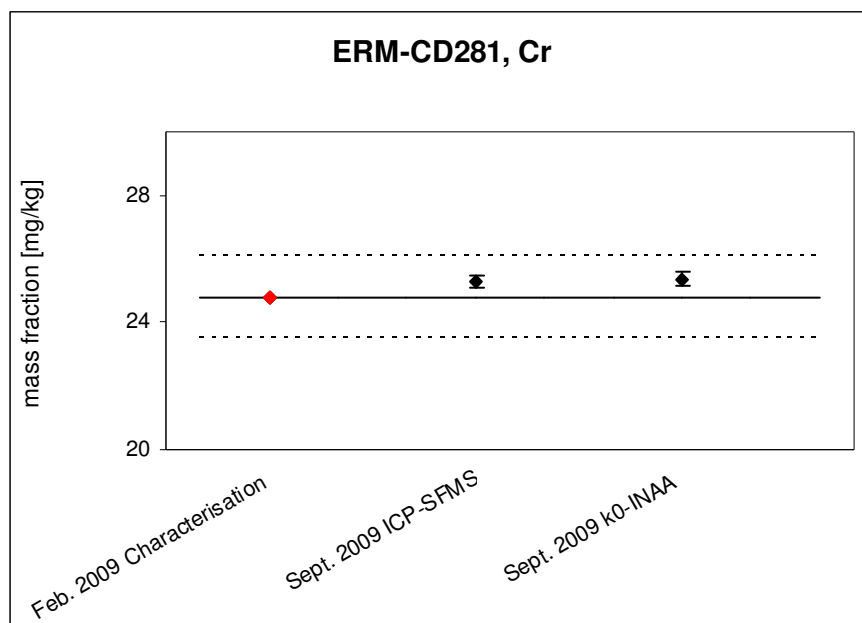
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



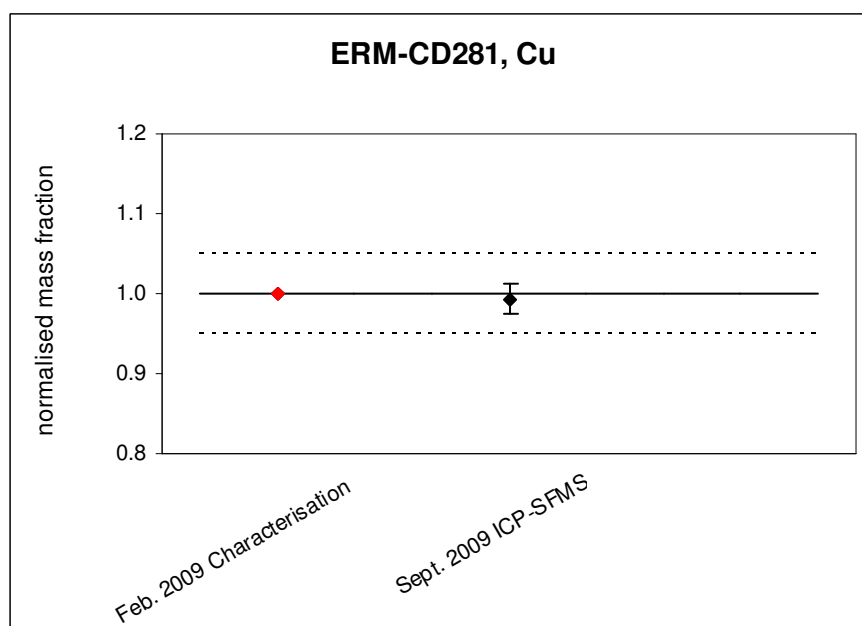
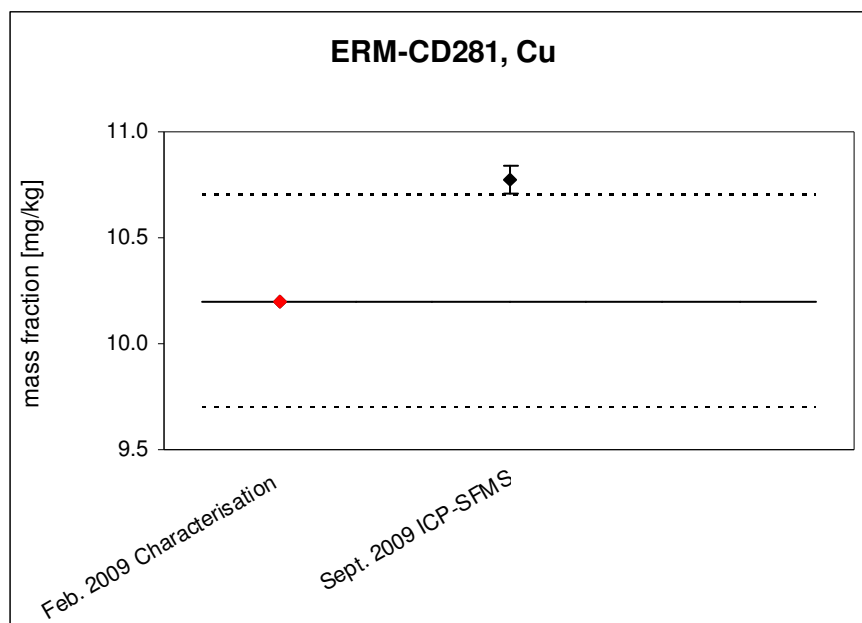
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



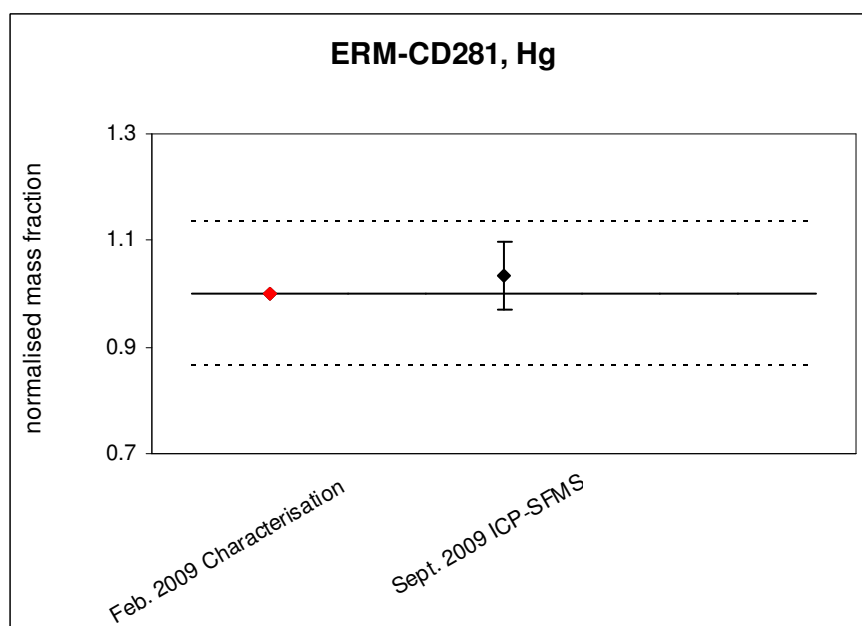
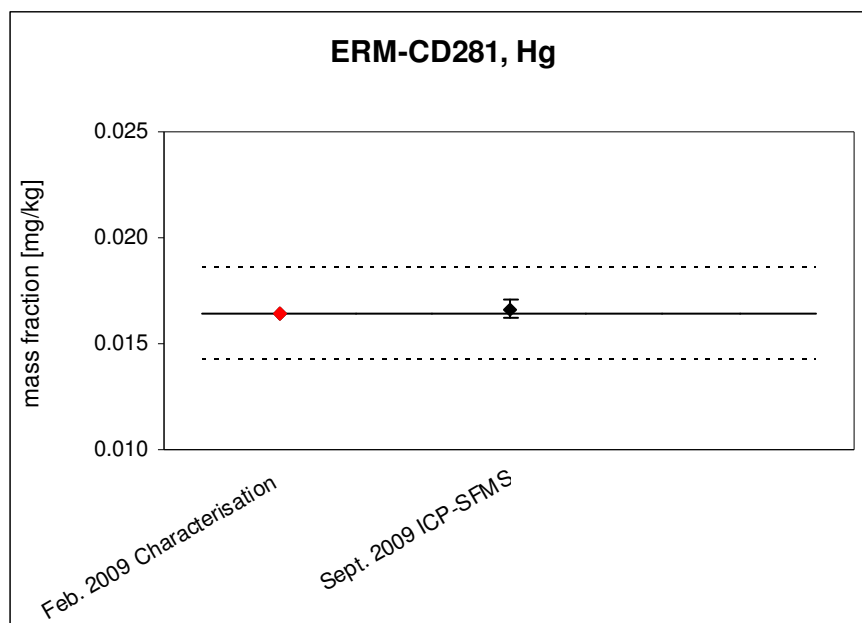
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



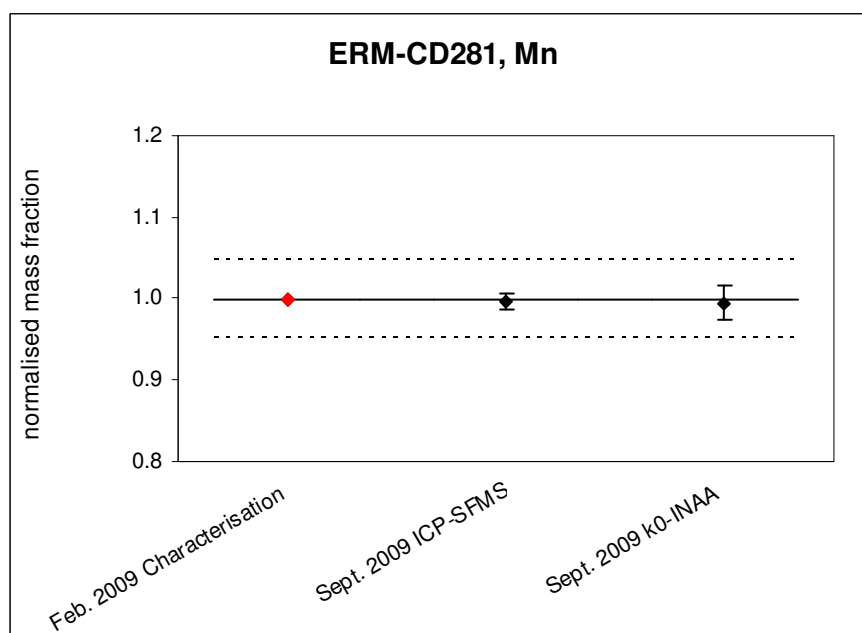
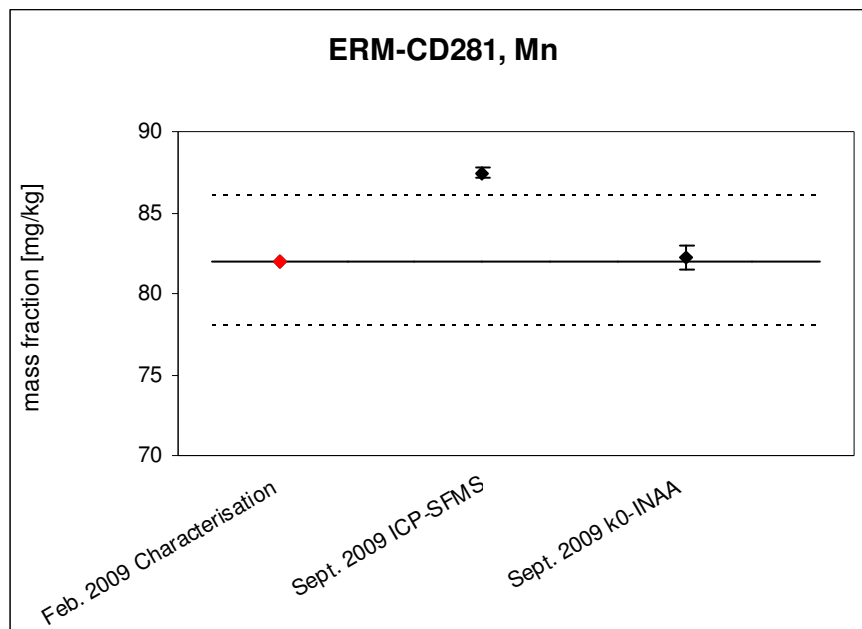
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



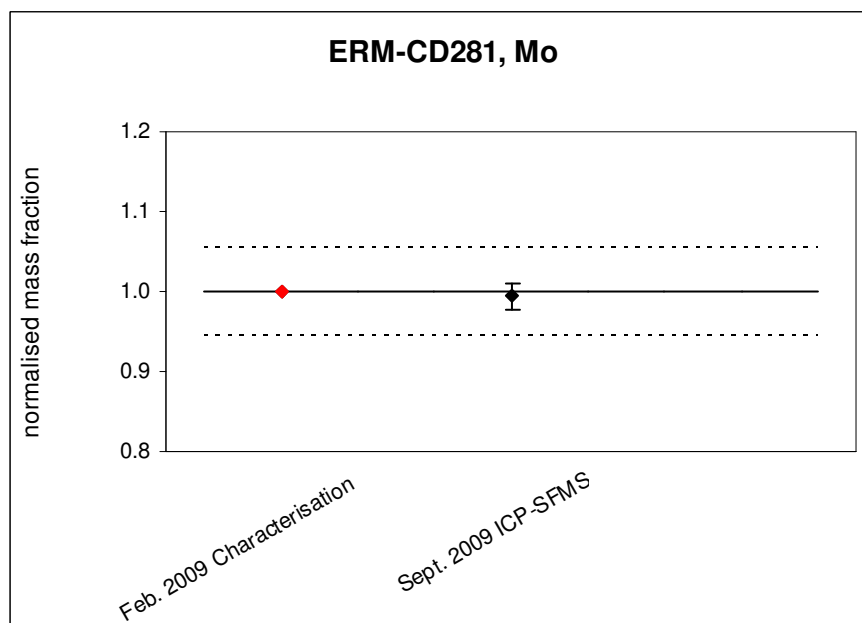
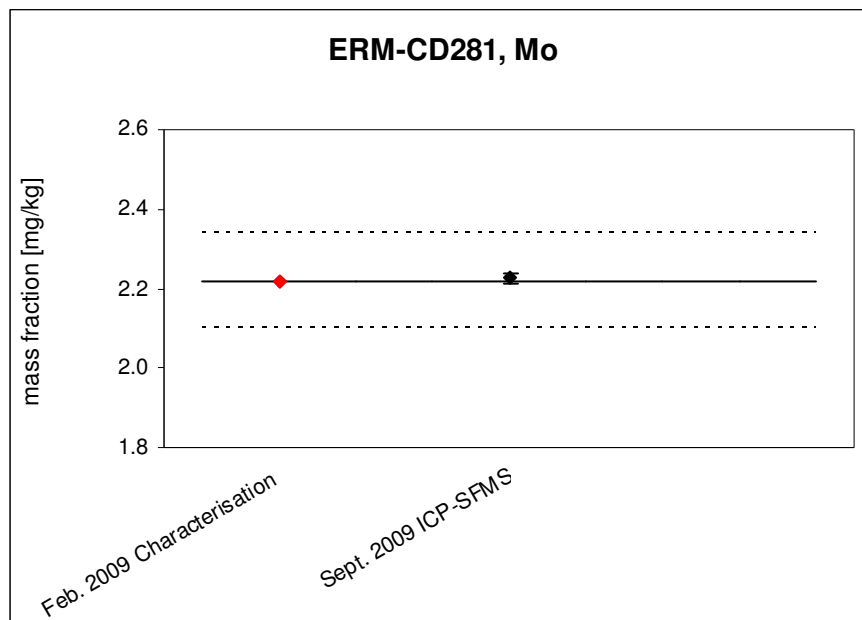
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



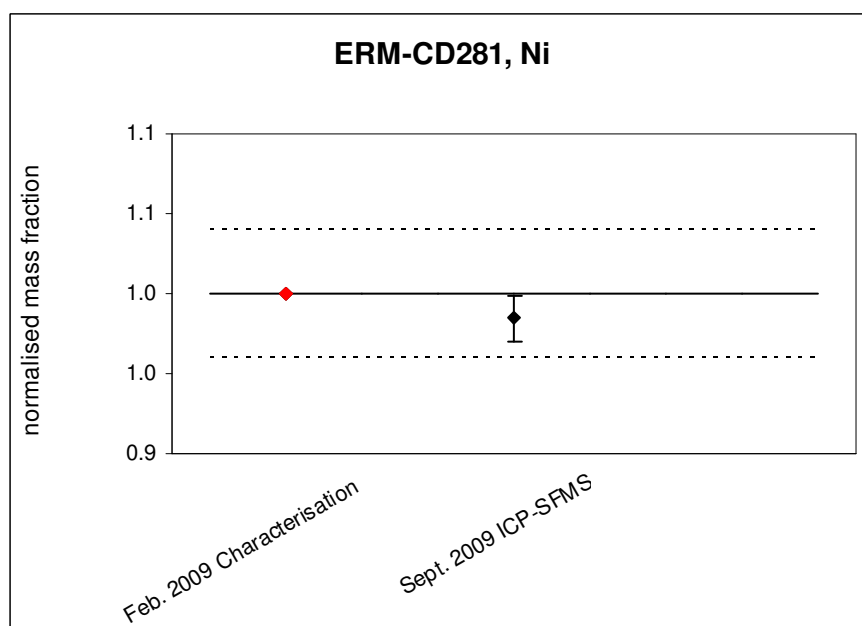
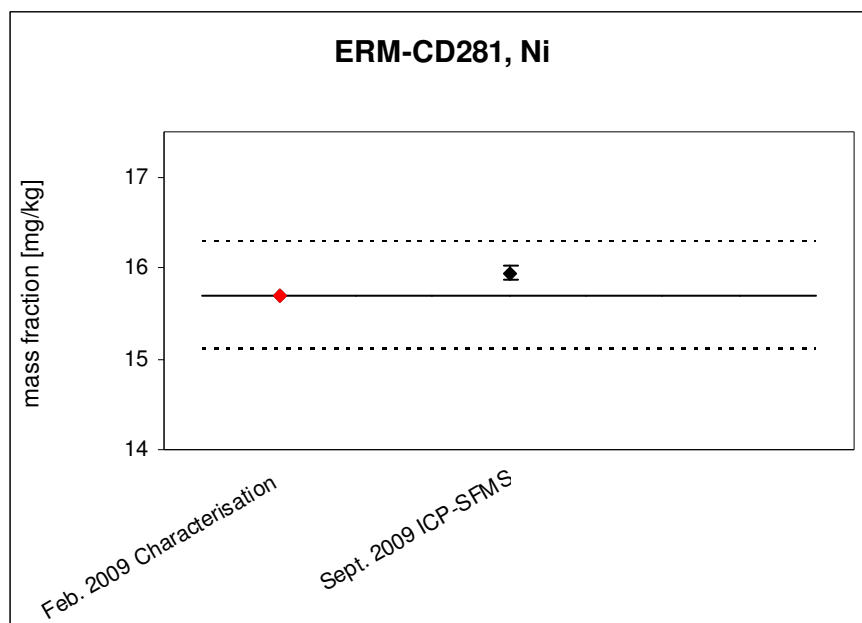
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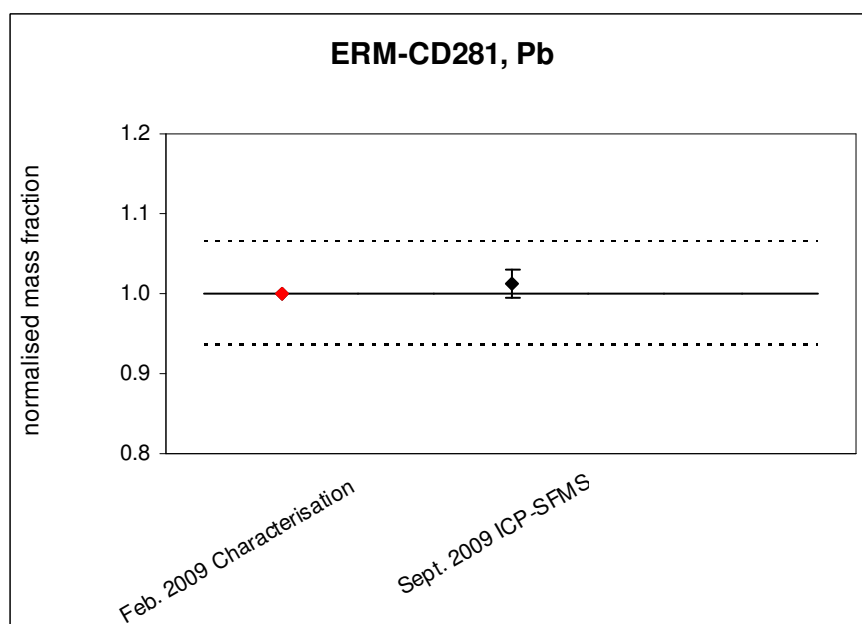
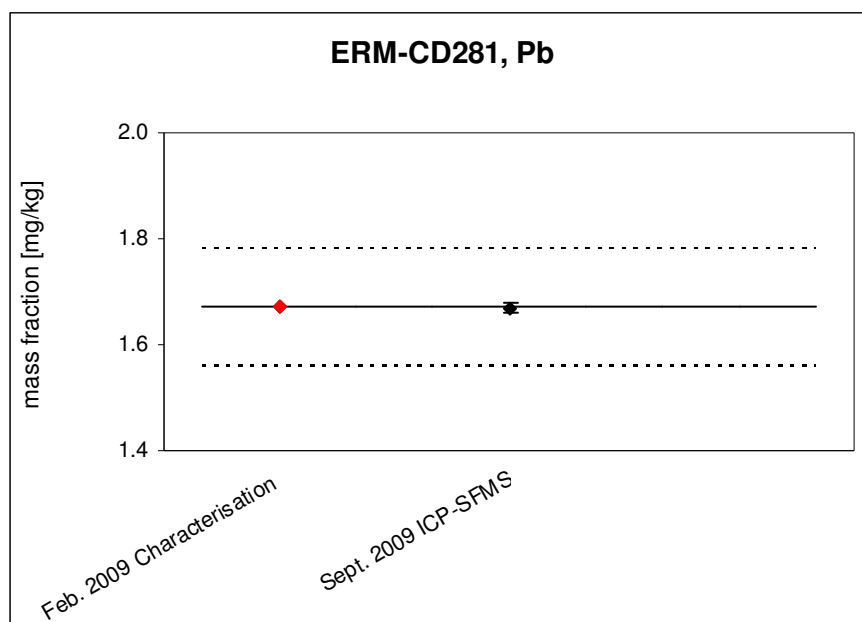
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



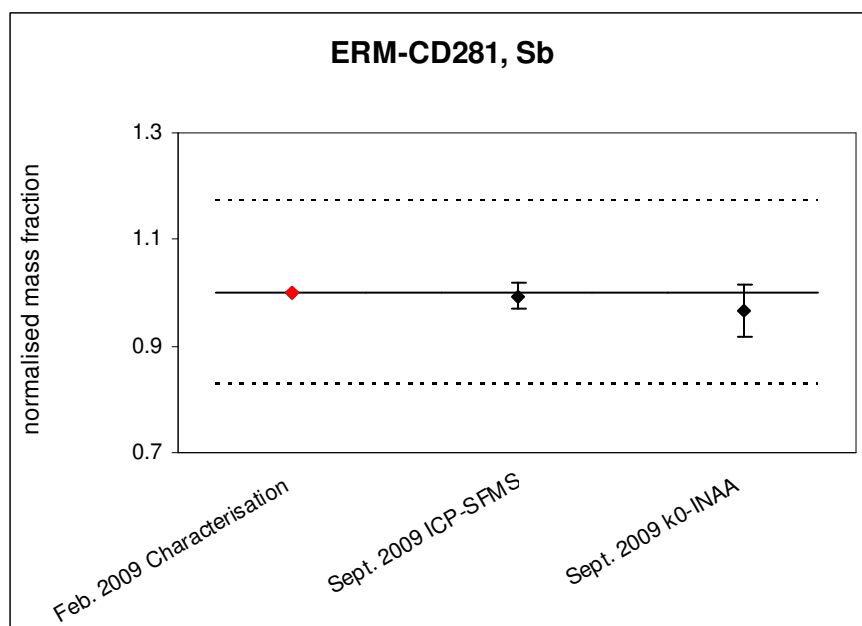
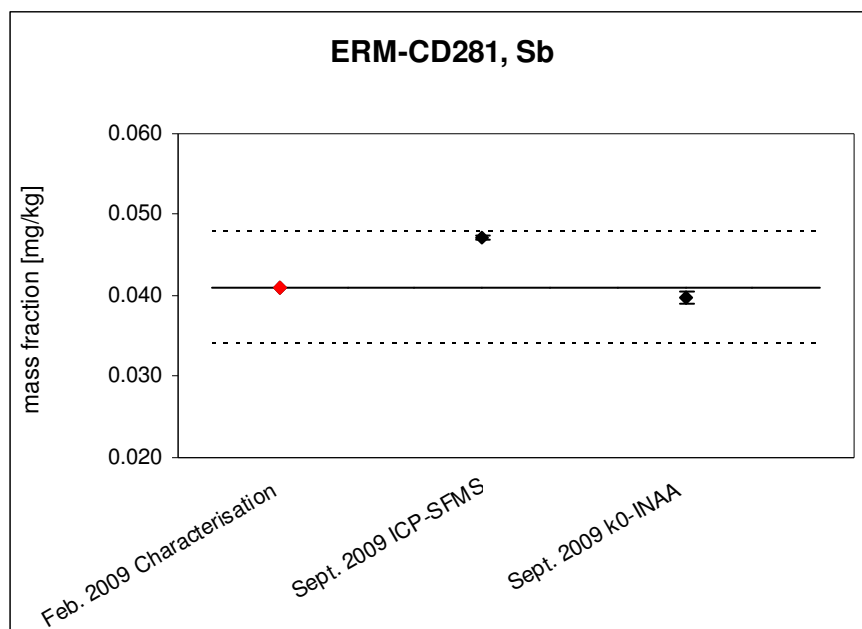
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



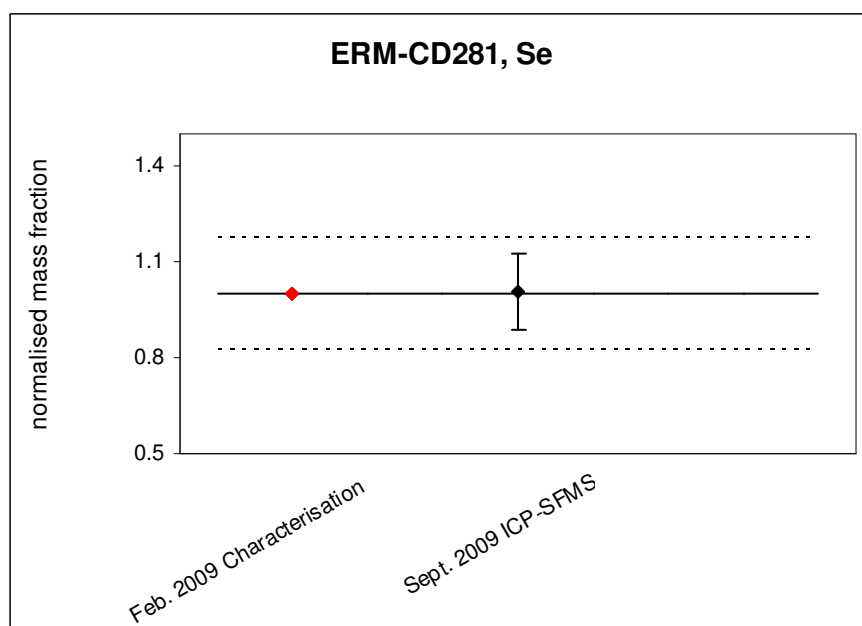
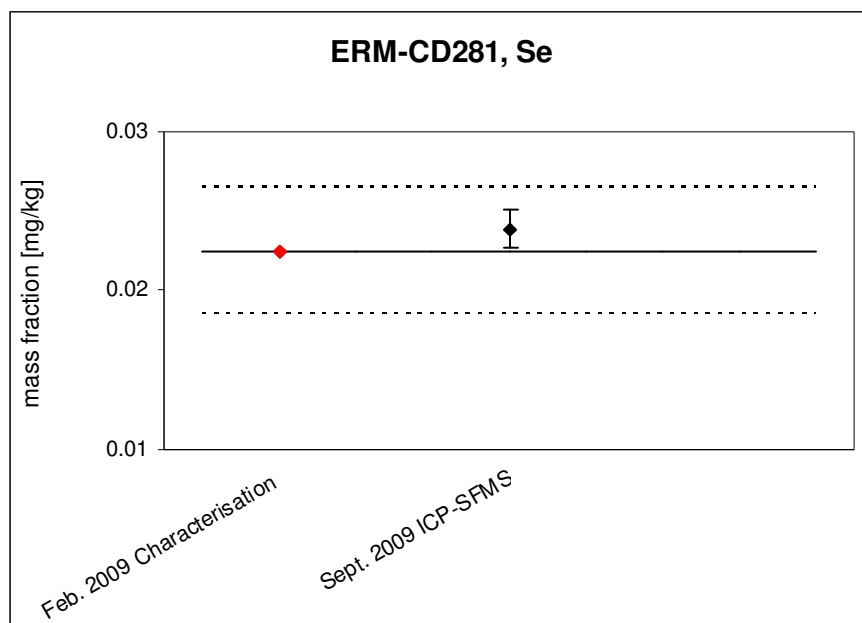
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



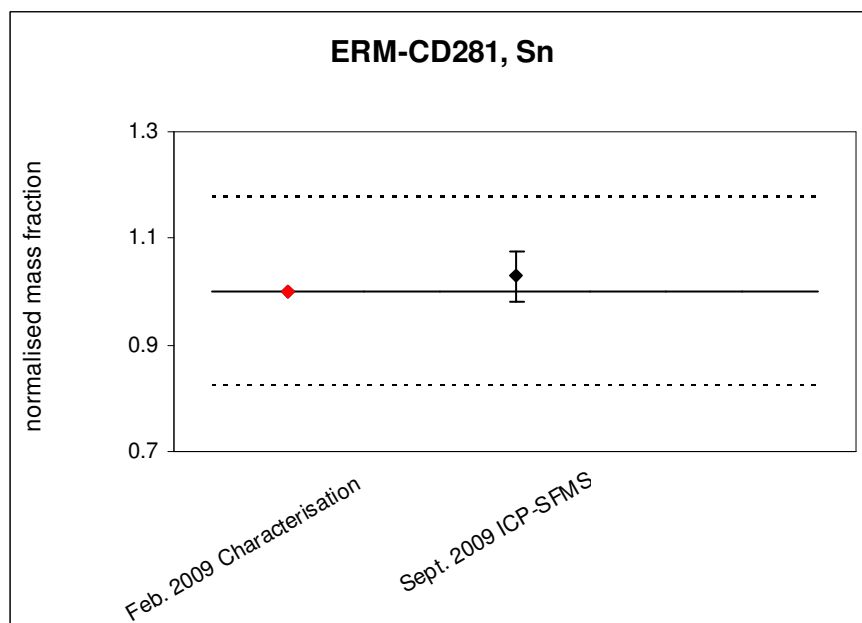
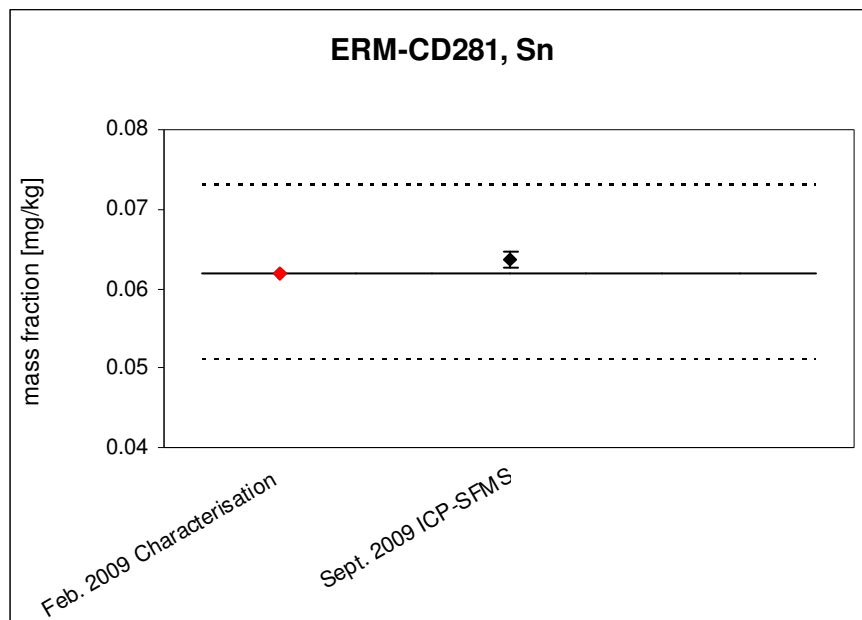
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



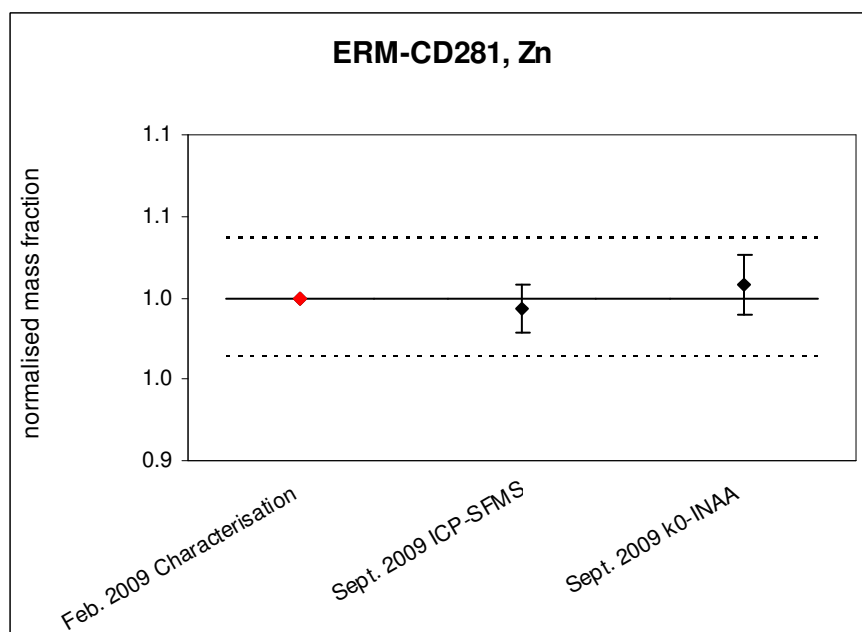
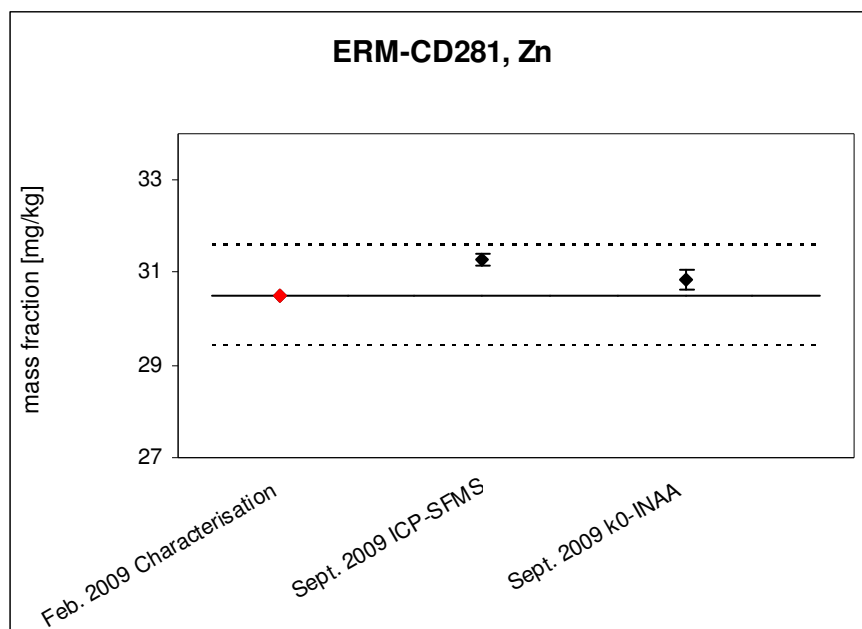
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Annex F: Summary of methods used in the characterisation

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-----------------|---------------------------|-----------------|---|---|---|
| L01a ICP-SFMS | All | 0.3 | Microwave assisted closed digestion using 5 mL HNO ₃ and 0.02 mL HF plus 0.2 mL HCl (Sb, Sn), heating at 170 °C for 60 min | Ultra Scientific (US) single element ICP standards QC: NIST 1547 | ICP- SFMS (Finnigan MAT, ELEMENT 2), two-points external calibration checked against synthetic QC sample at ½ max concentration, internal standard In or Lu, isotopes monitored: ⁷⁵ As, ⁹ B, ¹⁰ B, ¹¹¹ Cd, ¹¹⁴ Cd, ⁵² Cr, ⁵³ Cr, ⁶³ Cu, ⁶⁵ Cu, ²⁰¹ Hg, ²⁰² Hg, ⁵⁵ Mn, ⁹⁵ Mo, ⁹⁸ Mo, ⁶⁰ Ni, ²⁰⁶⁻²⁰⁸ Pb, ¹²³ Sb, ⁷⁸ Se, ¹²⁰ Sn, ⁶⁴ Zn and ⁶⁶ Zn, mass resolution: HR (As, Se), MR (Cr, Cu, Mn, Ni, Zn), LR (B, Cd, Hg, Mo, Pb, Sb, Sn), blank correction |
| L01b ICP-SFMS | As, Hg, Se | | Microwave assisted closed digestion using 5 mL HNO ₃ , 0.02 mL HF and 0.2 mL HCl, heating at 170 °C for 60 min | | ICP-SFMS (Finnigan MAT, ELEMENT 2), home made steady-state hydride generation (sodium borohydride), two-points external calibration checked against synthetic QC sample at ½ max concentration, internal standard In or Lu, isotopes monitored: ⁷⁵ As (HR), ^{201, 202} Hg (LR), ⁷⁸ Se (HR), blank correction |
| L01 ICP-OES | B, Cr, Cu, Mn, Ni, Pb, Zn | | Microwave assisted closed digestion using 5 mL HNO ₃ and 0.02 mL HF, heating at 170 °C for 60 min | | P-E Optima 4300DV (ICP-OES), two-points external calibration checked against synthetic QC sample at ½ max concentration, wavelengths [nm]: 249.677 (B), 205.56 (Cr), 324.752 (Cu), 257.61 (Mn), 231.604 (Ni), 220.353 (Pb), 213.857 (Zn), blank correction |
| L01 AFS | Hg, Se | | Microwave assisted closed digestion using 5 mL HNO ₃ , 0.02 mL HF and 0.2 mL HCl, heating at 170 °C for 60 min | | PSAnalytical M055B002 (AFS), two-points external calibration checked against synthetic QC sample at ½ max concentration, blank correction |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-------------------------|---------------------------------------|-----------------|---|---|---|
| L02 AFS | As, Sb, Se | 0.5 | Oven (Berghof DAB-3) digestion using 10 g of acid mixture (9.5 g HNO ₃ and 0.5 g HClO ₄), heating at 190 °C for 10 h, 0.5 mL HF added for resolving the possible residue | Single element standards CPI international or Inorganic Ventures QC: CRM281, NBS1572 | AFS with hydride generator (PSA), external calibration, wavelengths [nm]: 193.7 (As), 217.6 (Sb), 196 (Se) |
| L02 ICP-OES | B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Sn, Zn | | | | Varian Vista AX CCD simultaneous ICP-OES, external calibration with internal standard Ge or Lu, wavelengths [nm]: 249.678 (B), 214.439 (Cd), 267.716 (Cr), 327.395 (Cu), 257.61 (Mn), 202.032 (Mo), 231.604 (Ni), 220.353 (Pb), 189.927 (Sn), 206.2 (Zn) |
| L02 CV-AFS | Hg | | | | CV-AFS (PSA 10.025 Millennium Merlin), external calibration |
| L03 ICP-SFMS | As, B, Cd, Mo, Ni, Pb, Sb, Se, Sn | 1 | Closed microwave oven digestion using 6 mL HNO ₃ Suprapur and 2 mL HCl Suprapur, microwave oven program: 10 min ramp to 500 W, hold for 5 min at 500 W, 5 min ramp to 1000 W, hold 10 min at 1000 W, cool until < 50 °C, no residue left after digestion | Spex multielement solutions Merck single element solution (B) | ICP-SFMS (Thermo Finnigan Element 2), linear calibration with internal standard ¹⁰³ Rh, isotopes monitored: ⁷⁵ As, ⁹ B, ¹¹ B, ¹¹⁴ Cd (corrected for ¹¹⁸ Sn), ⁹⁸ Mo, ⁶⁰ Ni, ²⁰⁶⁻²⁰⁸ Pb, ¹²¹ Sb, ⁷⁸ Se, ¹¹⁸ Sn, mass resolution: HR (As, Se), MR (B, Cd, Mo, Ni, Pb, Sb, Sn), procedure blank |
| L03 CV-AFS | Hg | | | Merck single element solution | CV-A-AFS (Leeman Labs Inc. – Hydra AF Gold Plus), external linear calibration, wavelength 254 nm, procedure blank, measurements according to EPA Method 1631 |
| L04 k ₀ -NAA | Cr, Mn, Sb, Zn | 0.3 | No preparation | BCR 530 (Al 99,9%-Au 0,1%) flux monitor QC: NIST1633b; NIST1464a | 429 min irradiation with flux 3.0 x 10 ¹¹ neutrons/(cm ² s), decay time 14 days (Cr, Sb, Zn), 1 h (Mn), lines (keV): 320 (Cr), 847,1810 (Mn), 603,1691 (Sb), 1115 (Zn), isotope used: ⁵¹ Cr, ⁵⁶ Mn, ¹²⁴ Sb, ⁶⁵ Zn |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-----------------|---------------------------------------|-----------------|---|--|---|
| L05a ICP-QMS | As, Cr, Hg, Se | 0.5 | Closed vessel microwave digestion using 5 mL of mixture HNO ₃ and HCl (4:1), about 180 °C, 30 min, digests made up to 10 mL with deionised water, then 1 mL sample diluted 5-fold with HNO ₃ (1 % v/v) containing Rh as internal standard (12 µg/L), the same procedure for reagent blanks, CRMs, spiked samples and a spiked blank | SpectroSoL standard solutions QC: NIST 1515, NIST 1547, NIST 1548a | ICP-QMS (Agilent 7500ce ICP-MS), external calibration, isotopes monitored: ⁷⁵ As, ⁵² Cr, ²⁰² Hg, ⁷⁸ Se, CC mode: He (As, Cr), standard (Hg), H ₂ (Se), data correction for reagent blank and recovery of spike |
| L05b ICP-QMS | B, Cd, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Zn | | | Standard solutions (SpectroSoL, CertiPUR, ARISTAR) QC: NIST 1515, NIST 1547, NIST 1548a | ICP-QMS (Perkin Elmer Elan 6000 ICP-MS), external calibration, isotopes monitored: ¹¹ B, ¹¹¹ Cd, ⁶⁵ Cu, ⁵⁵ Mn, ⁹⁵ Mo, ⁶² Ni, ²⁰⁸ Pb, ¹²¹ Sb, ¹¹⁸ Sn, ⁶⁶ Zn, data correction for reagent blank and recovery of spike |
| L06 ICP-OES | B, Cr, Cu, Mn, Mo, Ni, Zn | 0.2 | Microwave digestion using 0.5 mL HCl suprapure and 5 mL HNO ₃ subboiled distilled, power ramp from 0 – 1440 W within 10 min, hold 1440 W for 10 min, then 0 W and cooling for 20 min | Spex multielement standards Traceability: check against certified single standard | ICP-OES (Spectro Ciros Vision), wavelengths (nm): 249.773 (B), 267.716 (Cr), 324.754 (Cu), 257.611 (Mn), 202.03 (Mo), 231.604 (Ni), 213.856 (Zn) |
| L06 ICP-QMS | As, Se, Sn | | Closed microwave digestion using 6 mL HNO ₃ + 1 mL HF, power: ramp 0-10 min: 0-1400 W; 10-20 min: 1400 W, pressure at 60 bar, temp at 200 °C, addition of 6 mL saturated boric acid solution, additional blank digestion for contamination control | Certified single element standard (Spex, CPI) BCR281 (QC) | ICP-QMS (ELAN DRC II, Perkin-Elmer – LAS), standard addition calibration with internal standard (Rh), isotopes monitored: ⁹¹ AsO, ⁸⁰ Se, ¹¹⁸ Sn, ¹²⁰ Sn, DRC mode: O ₂ (As), CH ₄ (Se, Sn), blank correction |
| L06 ICP-SFMS | | | | Traceability: check against assurance multi-element standard | ICP-SFMS (Element 1, Finnigan MAT), 7 point calibration curve with internal standard (Rh), isotopes monitored: ⁷⁵ As, ⁷⁷ Se, ⁸² Se, ¹²⁰ Sn, mass resolution: HR (As, Se) and LR (Sn) blank correction |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-------------------------|--|-----------------|--|---|--|
| L07 ICP-QMS | As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Zn | 0.2 0.5 (Sn) | EPA method 3052: <i>Microwave assisted acid digestion of siliceous and organically based matrices</i> using 9 mL HNO ₃ and 1 mL HF, 180 °C, 20 min | Single standards (Merck, Alfa Aesar, CPI) Traceability: NIST SRMs | ICP-QMS (Elan 6000, Perkin Elmer), external calibration with internal standard (Rn or Lu) for matrix-correction and spiking, isotopes monitored: ⁷⁵ As, ¹⁰⁻¹¹ B, ¹¹¹⁻¹¹³ Cd, ⁵³ Cr, ⁶³⁻⁶⁵ Cu, ²⁰⁰⁻²⁰² Hg, ⁵⁵ Mn, ⁹⁶⁻⁹⁸ Mo, ⁶⁰⁻⁶² Ni, ²⁰⁶⁻²⁰⁸ Pb, ¹²¹⁻¹²³ Sb, ⁶⁶⁻⁶⁸ Zn, blank correction |
| L07 ET-AAS | Se, Sn | | Sn: 10 mL H ₂ SO ₄ (9 N) and 5 mL HNO ₃ , heating at 275 °C for 2 h | | AAS (AAnalyst 200, Perkin Elmer), standard addition calibration, wavelengths [nm]: 196,0 (Se), 286.3 (Sn), slit 0.5 nm, blank correction |
| L07 k ₀ -NAA | As, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Sb, Se, Sn, Zn | 0.5 | No preparation | Au (IRMM-530) flux monitor | 240 min irradiation with flux 3.49 x 10 ¹¹ neutrons/(cm ² s), decay time: +/- 150 min to +/- 41 days, measuring time: 3600 s to +/- 95000 s, lines: 559.8 (As), 527.9 (Cd), 320.1 (Cr), 1345.8 (Cu), 279.2 (Hg), 846.8 (Mn), 140.5 (Mo), 1481.9 (Ni), 602.3/1691 (Sb), 136/264.7 (Se), 158.6 (Sn), 1115.5 (Zn), isotope used: ⁷⁶ As, ¹¹⁵ Cd, ⁵¹ Cr, ⁶⁴ Cu, ²⁰³ Hg, ⁵⁶ Mn, ^{99m} Tc, ⁶⁵ Ni, ¹²⁴ Sb, ⁷⁵ Se, ^{117m} Se, ⁶⁵ Zn |
| L08 ID ICP-QMS | Cd, Cu, Ni, Pb, Zn | 0.2 | Closed microwave oven digestion using 5 mL HNO ₃ , 1 mL H ₂ O ₂ and 0.15 mL HF, heating: 10 min (280 W), 5 min (0 W), 10 min (550 W), 5 min (0 W), 6 min (720 W), 7 min (0 W) and 10 min (280 W), blends between sample and spike prepared gravimetrically, before digestion sample spiking | Spike: ¹¹¹ Cd, ⁶⁵ Cu, ⁶¹ Ni, ²⁰⁶ Pb, ⁸² Se, ⁶⁷ Zn, concentrations by reverse ID | ICP-QMS (VG PQ Excell, Thermo Electron), double ID, isotopes monitored: ^{112/111} Cd, ^{63/65} Cu, ^{61/60} Ni, ^{208/206} Pb, ^{68/67} Zn, ratio measurements on two working isotopes, correction for: Mo interference (Cd), for matrix background (Cu, Ni, Zn), for blank (Pb) |
| L08 ID ICP-SFMS | Se | 0.4 | | | ICP- SFMS (VG Axiom, Thermo Electron), double ID, isotopes monitored: ^{82/80} Se (LR), ratio measurements on two working isotopes, CCT mode: mixture of He and H ₂ , correction for blank |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-----------------|-----------------------------------|-----------------|--|---|--|
| L09 ICP-QMS | B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn | 0.2 | Microwave assisted digestion using 8 mL HNO ₃ , 1 mL HCl and 2 mL HF, 200 °C, 45 min | Baker Instra Analyzed ICP Standards | ICP-QMS (Perkin Elmer Elan DRC II), external calibration with internal standards (Be, Ge, Y, In, Re) and matrix matched standards, isotopes monitored: ¹¹ B, ¹¹⁴ Cd, ⁵² Cr, ⁶⁵ Cu, ⁵⁵ Mn, ⁹⁸ Mo, ⁶⁰ Ni, ²⁰⁸ Pb, ⁶⁴ Zn |
| L09 CV-AAS | Hg | | B, Hg: 8 mL HNO ₃ and 1 mL HCl | CRM 281 No 743 (QC) | CV-AAS (Perkin Elmer FIMS 400), external calibration and matrix matched standards, reductant for cold vapour generation 0.2 % NaBH ₄ and 3 % HCl, wavelength 253.7 nm, slit 0.7 nm |
| L10 HG-AFS | As, Sb | 0.4 | Microwave assisted digestion using 2 mL ultrapure water (Milli-Q, 18.2 Mohm cm), 4 mL HNO ₃ (69 % m/m) and 2 mL H ₂ O ₂ (33 % m/m), heating to 90 °C in 1 min and 30 s, to 200 °C in 12 min, at 200 °C for 15 min | As ₂ O ₅ , Hg(NO ₃) ₂ , Mn(NO ₃) ₂ (Panreac) | HG-AFS (Millenium 10055 PS Analytical), external calibration, wavelengths [nm]: 193.7 (As), 217.6 (Sb), blank correction |
| L10 ET-AAS | B, Cd, Mo, Pb, Se, Sn | | | H ₃ BO ₃ , CdCl ₂ , Cr(NO ₃) ₃ , (NH ₄) ₆ Mo ₇ O ₂₄ , SnCl ₄ , Zn(NO ₃) ₂ SeO ₂ (Merck) | 1100 ET-AAS coupled with HGA 700 and AS70 autosampler Perkin Elmer), deuterium background correction, external calibration, wavelengths (nm): 249.7 (B), 228.8 (Cd), 313.3 (Mo), 283.3 (Pb), 224.6 (Sn), slit 0.7 nm, blank correction |
| L10 ICP-OES | Cr, Cu, Mn, Ni, Zn | | | Cu(NO ₃) ₂ , Ni(NO ₃) ₂ Pb(NO ₃) ₂ (Scharlau) | Se: 4110ZL ET-AAS coupled with TGHA and AS 71 autosampler, Perkin Elmer, Zeeman background correction, external calibration, wavelength 196 nm, slit 0.7 nm, blank correction |
| L10 CV-AAS | Hg | | | K[Sb(OH) ₆] (Aldrich) | ICP-OES (Optima 3300 DV Perkin Elmer), background correction, external calibration, wavelengths (nm): 267.716 (Cr), 324.752 (Cu), 257.61 (Mn), 231.604 (Ni), 213.857 (Zn), blank correction |
| | | | | | CV-AAS (FIAS 400 coupled with 4110ZL spectrometer and AS 71 autosampler, Perkin Elmer), external calibration, wavelength 253.7 nm, slit 0.7 nm, blank correction |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-----------------|---------------------------------|---------------------|--|----------------------------|--|
| L11 DMA | Hg | 0.05 | No preparation | JSI standard solution | DMA (Milestone Srl.), decomposition temperature 650 °C, wavelength 254 nm |
| L11 CV-AAS | | 0.2 | Closed Teflon vessels digestion using 4 mL HNO ₃ , heating at 100 °C for 12 h | | CV-AAS (LDC Milton Roy), wavelength 253.7 nm, blank correction |
| L11 ET-AAS | Cd, Cr, Cu, Ni, Pb | 0.35 | Closed vessel microwave digestion using 4 mL HNO ₃ (s.p.) and 0.1 mL HF (s.p.), heating to 180 °C in 20 min, hold 20 min, the same procedure applied for blanks | Merck standard solutions | ET-AAS (Hitachi Z-8270 polarized Zeeman AAS), external calibration, Zeeman background correction, wavelengths [nm]: 228.8 (Cd), 359.3 (Cr), 324.8 (Cu), 323 (Ni), 283.3 (Pb), slit 1.3 nm and 0.2 nm (Ni) |
| L11 FAAS | Mn, Zn | | | | FAAS (Varian, Spectra AA110), external calibration, deuterium background correction, wavelengths [nm]: 324.8 (Mn), 324.8 (Zn), nitrous oxide-acetylene flame (Mn) and air-acetylene flame (Zn) |
| L11 ICP-QMS | Cr, Cu, Mn, Mo, Ni, Pb, Sb, Zn, | | | | ICP-QMS (Agilent, ICP-MS 7500ce), external calibration, CC mode: He (Cr, Mo), H ₂ (Sb), isotopes monitored: ⁵² Cr, ⁶³ Cu, ⁵⁵ Mn, ⁹⁵ Mo, ⁶⁰ Ni, ²⁰⁶⁻²⁰⁸ Pb, ¹²¹ Sb, ⁶⁶ Zn |
| L11 RNAA | As, Se | 0.2, 0.2 - 0.4 (Se) | No sample preparation before irradiation. Digestion and separation of the sample was done after irradiation | Merck ICP single standards | 20 h (As) and 40 h (Se) irradiation, with flux 1.10×10^{12} neutrons/(cm ² s), decay time (days): 2 - 3 (As), 14 - 20 (Se), measuring time (h): 1 - 2 (As), 14 -20 (Se), lines (keV): 559.1 (As), 400.7 (Se), isotope used: : ⁷⁶ As, ⁷⁵ Se |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|--------------------------|--------------------|-----------------|--|--|---|
| L11 k ₀ -INAA | Cr, Mn, Mo, Sb, Zn | 0.2 | No preparation | flux monitors: Al-Au (0.1 %), Zn (99.99 %), Zr (99.8 %) NIST 1547 Peach Leaves (QC) Validated using BCR CRMs (different matrices) | 7 and 1200 min irradiation with flux 1.10×10^{12} neutrons/(cm ² s), decay time: 30 - 36 days (Cr, Sb, Zn), 2 h (Mn), 8 - 12 days (Mo), measuring time: 16 h (Cr, Sb, Zn), 25 min (Mn), 15 h (Mo), lines (keV): 320.1 (Cr), 846.8 (Mn), 140.5 (Mo), 602.7 (Sb), 1115.5 (Zn), isotope used: ⁵¹ Cr, ⁵⁶ Mn, ^{99m} Tc, ¹²⁴ Sb, ⁶⁵ Zn |
| L12 ICP-QMS | As, Se, Sn | 2 | Closed microwave digestion using 2 mL HF and 4.5 mL HNO ₃ , 240 °C, 50 min, centrifugation | Metal salts in acids (VWR) | ICP-QMS (Perkin Elmer Elan DRC II), external calibration (linear regression through zero) with internal standard (Rh), isotopes monitored: ⁷⁵ As, ⁷⁸ Se, ¹¹⁸ Sn, LR (all elements), DRC mode: standard (As, Se), NH ₃ (Se) |
| L13 ICP-QMS | As, Sn | 0.5 | Digestion according to SS-EN ISO 15587-2, closed microwave digestion using 15 mL HNO ₃ and 1 mL H ₂ O ₂ , 170 °C, 10 min, predigestion open system 100 °C | Multi 3 ICP-MS, Multi 4 ICP-MS (PerkinElmer) | ICP-QMS (Perkin Elmer ELAN DRC-e), internal calibration (linear through zero), Internal standards ¹⁰³ Rh (As) and ¹¹⁵ In (Sn), isotopes monitored: ⁷⁵ As, ¹¹⁸ Sn, ¹²⁰ Sn, DRC mode: NH ₄ , blank correction (Sn) |
| L14 ICP-QMS | As | 0.5 | Microwave digestion using 10 mL HNO ₃ (7 M), 180 °C, 37 min, filtration | ICP multielement standard VI for MS (AccuStandard Inc.) NIST 1568a Rice flour (QC) | ICP-QMS (Elan 6000 Perkin Elmer), isotope monitored ⁷⁵ As, standard addition calibration, blank correction |

| Lab-method code | Elements | Sample mass [g] | Sample preparation | Calibrants | Instrumentation and measurement method |
|-----------------|----------|-----------------|--|---------------------------------------|--|
| L15 ID ICP-SFMS | Se, Sn | 0.5 | Sample weighing, spiking (^{77}Se or ^{117}Sn), microwave digestion using 3 mL HNO_3 , 2 mL H_2O_2 and 1 mL HCl , 185 °C, 35 min | NIST SRM3149 (Se), NIST SRM3161a (Sn) | ICP-SFMS (ThermoFisher Scientific), acid matrix of calibration standards, isotopes monitored: $^{77, 78, 82}\text{Se}$ (HR) and $^{117, 118, 120}\text{Sn}$ (MR) |
| L16 ID ICP-SFMS | Sn | 0.5 | High pressure asher digestion using 3 mL HCl and 2 mL HNO_3 , 320 °C, 240 min (150 min at 320 °C), trace-matrix separation with Truspec resin | Sn metal (BAM) | ICP-QMS (Element XR, Thermo Fisher Scientific), isotope monitored ^{117}Sn , blank correction |

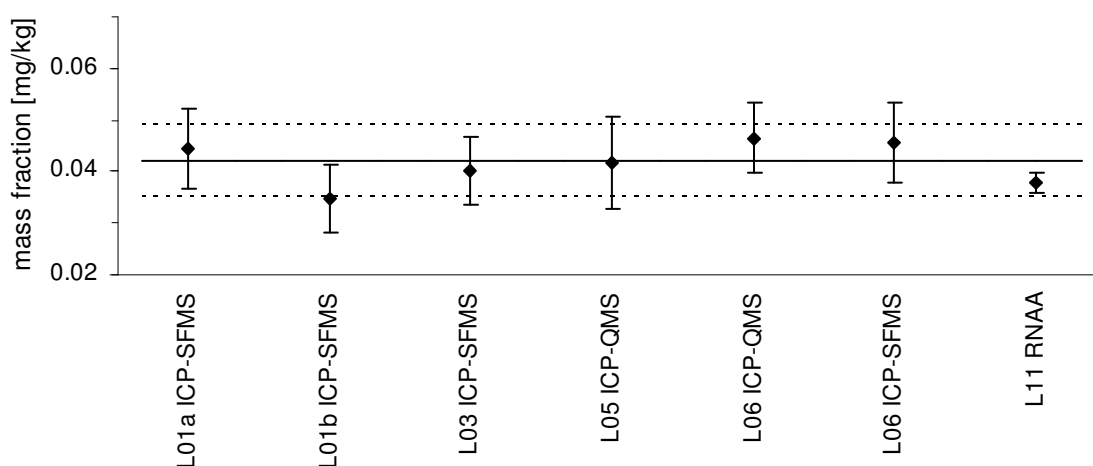
Annex G: Results of the characterisation measurements

ERM-CD281, As

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|---------|---------|---------|---------|---------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 0.0522 | 0.0497 | 0.0496 | 0.0514 | 0.0593 | 0.0478 | 0.0443 | 0.0081 |
| | 0.0358 | 0.038 | 0.0372 | 0.0359 | 0.0373 | 0.0379 | | |
| L01b ICP-SFMS | 0.0348 | 0.0362 | 0.034 | 0.0339 | 0.0327 | 0.0366 | 0.0347 | 0.0015 |
| L03 ICP-SFMS | 0.0423 | 0.0402 | 0.0389 | 0.0410 | 0.0394 | 0.0395 | 0.0402 | 0.0013 |
| L05 ICP-QMS | 0.039 | 0.048 | 0.039 | 0.039 | 0.041 | 0.044 | 0.0417 | 0.0037 |
| L06 ICP-QMS | 0.05236 | 0.04658 | 0.04474 | 0.04474 | 0.04546 | 0.04519 | 0.04651 | 0.00294 |
| L06 ICP-SFMS | 0.05390 | 0.04298 | 0.04364 | 0.04406 | 0.04454 | 0.04399 | 0.04552 | 0.00414 |
| L11 RNAA | 0.0344 | 0.0344 | 0.0425 | 0.0361 | 0.0365 | 0.0427 | 0.0378 | 0.0038 |
| Excluded results ^a | | | | | | | | |
| L02 AFS | 0.060 | 0.037 | 0.033 | 0.060 | 0.018 | 0.060 | 0.045 | 0.018 |
| L07 ICP-QMS | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | | |
| L07 k ₀ -NAA | < 0.2 | < 0.2 | < 0.2 | < 0.3 | < 0.2 | < 0.2 | | |
| L10 HG-AFS | 0.21 | 0.16 | 0.10 | 0.21 | 0.15 | 0.12 | 0.16 | 0.05 |
| L12 ICP-QMS | 0.17 | 0.20 | 0.17 | 0.14 | 0.13 | 0.15 | 0.16 | 0.03 |
| L13 ICP-QMS | 0.072 | 0.121 | 0.059 | 0.063 | 0.089 | 0.056 | 0.077 | 0.025 |
| L14 ICP-QMS | 0.056 | 0.055 | 0.064 | 0.052 | 0.064 | 0.063 | 0.059 | 0.005 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

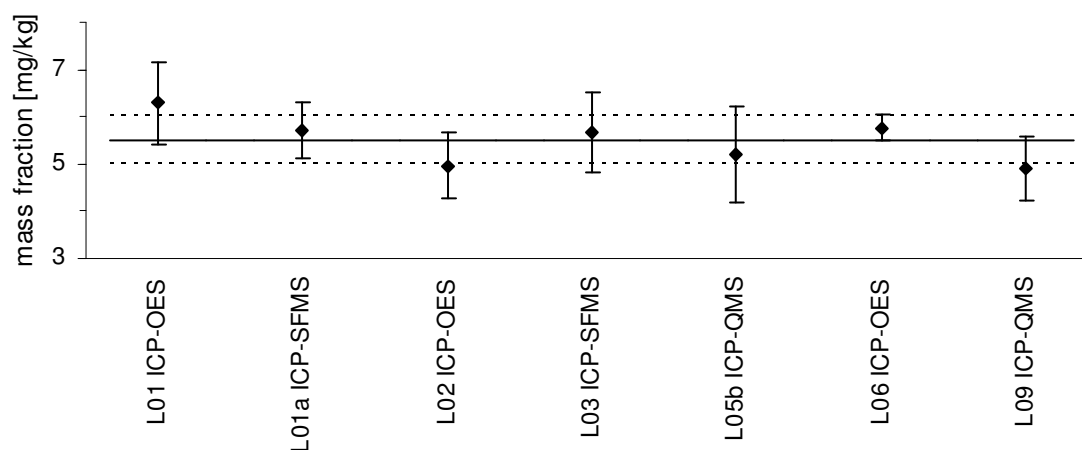


ERM-CD281, B

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|-------|-------|-------|-------|-------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01 ICP-OES | 6.33 | 6.44 | 6.14 | 6.31 | 6.44 | 6.05 | 6.29 | 0.16 |
| L01a ICP-SFMS | 5.82 | 5.58 | 5.77 | 5.82 | 5.65 | 5.59 | 5.71 | 0.11 |
| L02 ICP-OES | 4.931 | 4.947 | 5.000 | 4.939 | 4.986 | 4.982 | 4.964 | 0.029 |
| L03 ICP-SFMS | 5.643 | 5.539 | 5.568 | 5.549 | 5.563 | 6.099 | 5.660 | 0.218 |
| L05b ICP-QMS | 5.1 | 5.4 | 5.2 | 5.3 | 5.1 | 5.1 | 5.2 | 0.1 |
| L06 ICP-OES | 5.69 | 5.81 | 5.80 | 5.78 | 5.86 | 5.69 | 5.77 | 0.07 |
| L09 ICP-QMS | 5.02 | 4.84 | 4.84 | 5.16 | 4.69 | 4.97 | 4.92 | 0.16 |
| Excluded results ^a | | | | | | | | |
| L07 ICP-QMS | 7.55 | 6.22 | 5.11 | 8.72 | 5.22 | 7.61 | 6.74 | 1.45 |
| L10 ET-AAS | 5.2 | 12.5 | 5.1 | 4.7 | 16.0 | 7.7 | 8.5 | 4.7 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

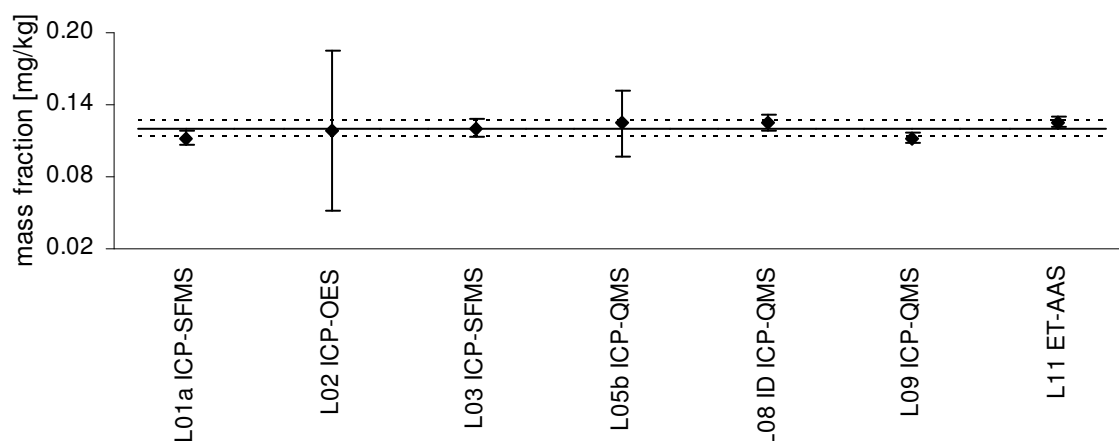


ERM-CD281, Cd

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|-------|-------|-------|-------|-------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 0.113 | 0.11 | 0.113 | 0.113 | 0.113 | 0.112 | 0.112 | 0.001 |
| L02 ICP-OES | 0.115 | 0.122 | 0.112 | 0.120 | 0.122 | 0.120 | 0.119 | 0.004 |
| L03 ICP-SFMS | 0.116 | 0.125 | 0.118 | 0.123 | 0.121 | 0.122 | 0.121 | 0.003 |
| L05b ICP-QMS | 0.128 | 0.126 | 0.121 | 0.127 | 0.123 | 0.121 | 0.124 | 0.003 |
| L08 ID ICP-QMS | 0.134 | 0.129 | 0.125 | 0.126 | 0.125 | 0.113 | 0.125 | 0.007 |
| L09 ICP-QMS | 0.121 | 0.111 | 0.108 | 0.11 | 0.108 | 0.114 | 0.112 | 0.005 |
| L11 ET-AAS | 0.127 | 0.127 | 0.123 | 0.130 | 0.125 | 0.123 | 0.126 | 0.003 |
| Excluded results ^a | | | | | | | | |
| L07 k_0 -NAA | < 1 | < 1.5 | < 1.5 | < 1.5 | < 1 | < 1.5 | | |
| L07 ICP-QMS | 0.15 | 0.12 | 0.13 | 0.16 | 0.13 | 0.15 | 0.14 | 0.02 |
| L10 ET-AAS | 0.165 | 0.156 | 0.149 | 0.171 | 0.152 | 0.157 | 0.158 | 0.008 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



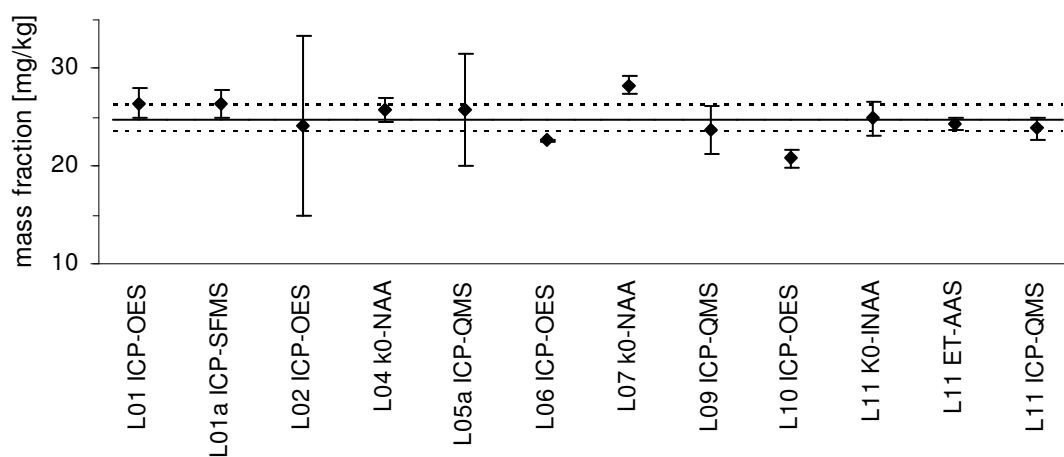
ERM-CD281, Cr

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|--------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01 ICP-OES | 26.2 | 26.2 | 26.1 | 27.0 | 26.5 | 26.8 | 26.5 | 0.4 |
| L01a ICP-SFMS | 26.6 | 26.1 | 25.9 | 26.7 | 27.0 | 26.4 | 26.5 | 0.404 |
| L02 ICP-OES | 24.117 | 24.005 | 24.208 | 24.212 | 24.302 | 24.258 | 24.184 | 0.107 |
| L04 k ₀ -NAA | 26.11 | 25.14 | 26.17 | 25.85 | 25.61 | 25.86 | 25.79 | 0.38 |
| L05a ICP-QMS | 24.9 | 25.4 | 25.9 | 25.4 | 26.2 | 27.0 | 25.8 | 0.7 |
| L06 ICP-OES | 22.4 | 22.8 | 22.6 | 22.9 | 22.4 | 22.7 | 22.6 | 0.2 |
| L07 k ₀ -NAA | 29 | 28 | 28 | 29 | 28 | 28 | 28 | 1 |
| L09 ICP-QMS | 24.24 | 25.01 | 24.06 | 23.07 | 22.94 | 22.74 | 23.68 | 0.90 |
| L10 ICP-OES | 21.08 | 20.15 | 21.13 | 20.13 | 19.95 | 22.22 | 20.78 | 0.87 |
| L11 K ₀ -INAA | 25.4 | 24.8 | 24.8 | 24.6 | 24.8 | 24.8 | 24.9 | 0.3 |
| L11 ET-AAS | 25.1 | 24.2 | 23.9 | 25.2 | 24.1 | 24.0 | 24.4 | 0.6 |
| L11 ICP-QMS | 24.6 | 23.3 | 24.3 | 23.3 | 23.9 | 23.6 | 23.8 | 0.5 |

| Excluded results ^a | | | | | | | | |
|-------------------------------|------|------|------|------|------|------|------|-----|
| L07 ICP-QMS | 32.3 | 26.8 | 27.1 | 31.9 | 27.0 | 31.0 | 29.4 | 2.6 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

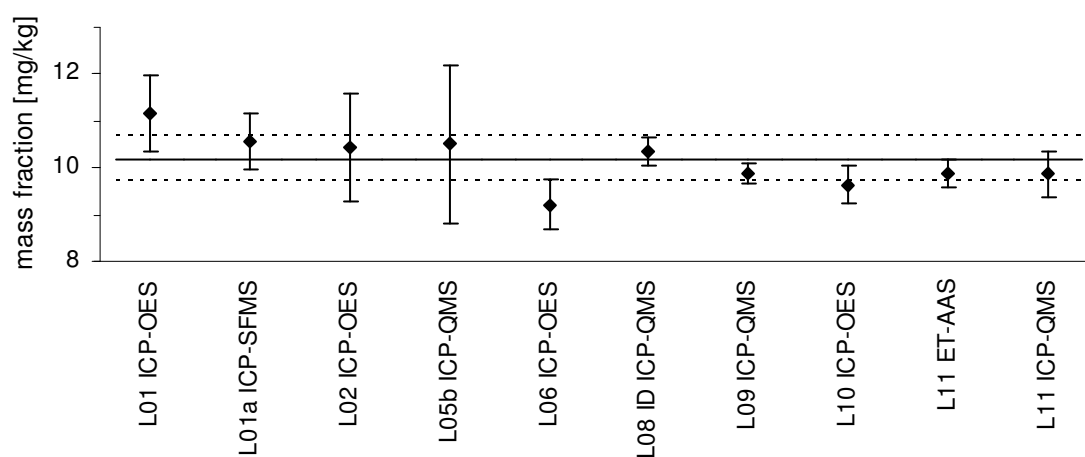


ERM-CD281, Cu

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01 ICP-OES | 11.1 | 11.1 | 11.2 | 11.2 | 11.2 | 11.2 | 11.2 | 0.1 |
| L01a ICP-SFMS | 10.8 | 10.5 | 10.4 | 10.7 | 10.6 | 10.4 | 10.6 | 0.2 |
| L02 ICP-OES | 10.190 | 10.238 | 10.568 | 10.364 | 10.580 | 10.658 | 10.433 | 0.196 |
| L05b ICP-QMS | 10.51 | 10.77 | 10.54 | 10.36 | 10.56 | 10.27 | 10.50 | 0.17 |
| L06 ICP-OES | 9.05 | 9.56 | 9.27 | 9.25 | 9.06 | 9.11 | 9.22 | 0.19 |
| L08 ID ICP-QMS | 10.483 | 10.412 | 10.615 | 10.143 | 10.605 | 9.934 | 10.365 | 0.272 |
| L09 ICP-QMS | 9.84 | 10.19 | 10.00 | 9.83 | 9.85 | 9.63 | 9.89 | 0.19 |
| L10 ICP-OES | 10.3 | 9.61 | 9.57 | 9.75 | 9.03 | 9.57 | 9.64 | 0.41 |
| L11 ET-AAS | 10.10 | 9.86 | 9.62 | 10.10 | 9.67 | 9.86 | 9.87 | 0.20 |
| L11 ICP-QMS | 9.74 | 9.94 | 9.74 | 9.97 | 9.87 | 9.97 | 9.87 | 0.11 |
| Excluded results ^a | | | | | | | | |
| L07 k ₀ -NAA | < 150 | < 200 | < 100 | < 100 | < 200 | < 150 | | |
| L07 ICP-QMS | 13.3 | 11.0 | 11.4 | 11.6 | 11.4 | 13.5 | 12.0 | 1.1 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

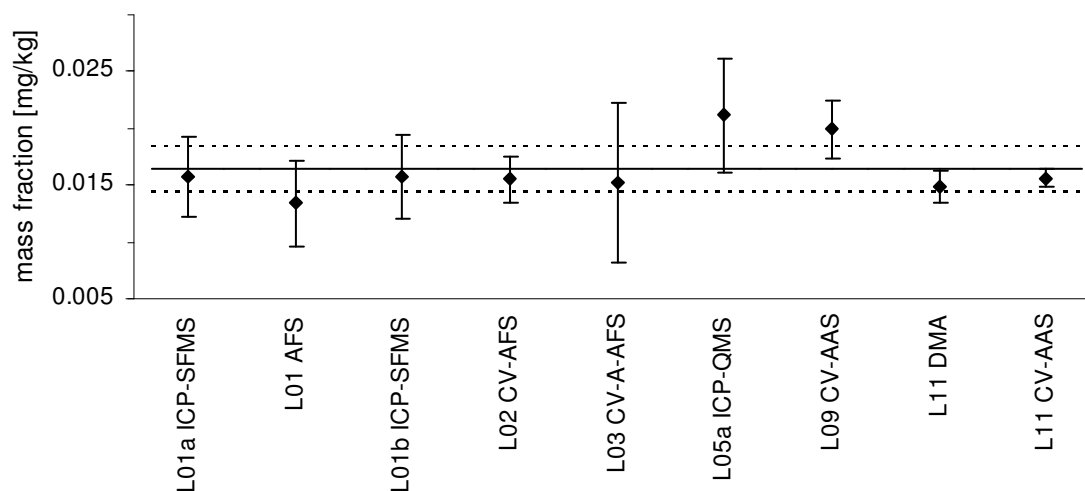


ERM-CD281, Hg

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 0.0173 | 0.0174 | 0.0169 | 0.0180 | 0.0174 | 0.0180 | 0.0158 | 0.0019 |
| | 0.0133 | 0.0131 | 0.0140 | 0.0145 | 0.0145 | 0.0146 | | |
| L01 AFS | 0.0138 | 0.0124 | 0.0130 | 0.0145 | 0.0126 | 0.0139 | 0.0134 | 0.0008 |
| L01b ICP-SFMS | 0.0149 | 0.0156 | 0.0159 | 0.0159 | 0.0160 | 0.0162 | 0.0158 | 0.0005 |
| L02 CV-AFS | 0.016 | 0.016 | 0.016 | 0.016 | 0.015 | 0.014 | 0.016 | 0.001 |
| L03 CV-A-AFS | 0.0158 | 0.0158 | 0.0150 | 0.0149 | 0.0157 | 0.0141 | 0.0152 | 0.0007 |
| L05a ICP-QMS | 0.023 | 0.022 | 0.019 | 0.022 | 0.021 | 0.020 | 0.021 | 0.001 |
| L09 CV-AAS | 0.0215 | 0.0191 | 0.0197 | 0.0190 | 0.0195 | 0.0206 | 0.0199 | 0.0010 |
| L11 DMA | 0.0143 | 0.0132 | 0.0174 | 0.0143 | 0.0150 | 0.0146 | 0.0148 | 0.0014 |
| L11 CV-AAS | 0.0162 | 0.0160 | 0.0152 | 0.0155 | 0.0156 | 0.0154 | 0.0157 | 0.0004 |
| Excluded results ^a | | | | | | | | |
| L07 k ₀ -NAA | < 0.07 | < 0.07 | < 0.09 | < 0.09 | < 0.07 | < 0.08 | | |
| L07 ICP-QMS | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | | |
| L10 CV-AAS | 0.0398 | 0.0249 | 0.0401 | 0.0616 | 0.046 | 0.0289 | 0.0205 | 0.0402 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



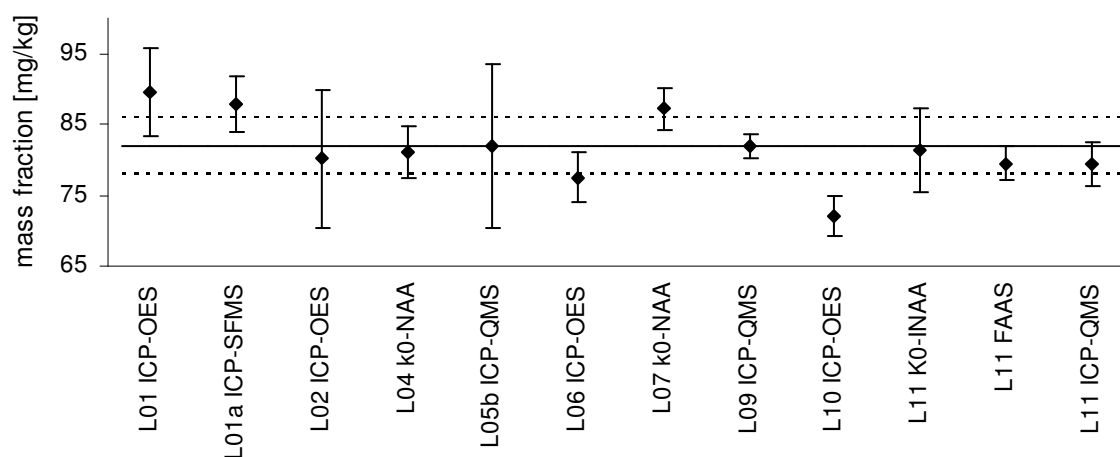
ERM-CD281, Mn

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|--------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01 ICP-OES | 88.4 | 89.4 | 89.3 | 90.2 | 90.4 | 89.7 | 89.6 | 0.7 |
| L01a ICP-SFMS | 88.8 | 86.4 | 88.2 | 89.5 | 88.6 | 86.3 | 88.0 | 1.3 |
| L02 ICP-OES | 80.181 | 79.585 | 80.283 | 79.680 | 80.237 | 80.697 | 80.111 | 0.414 |
| L04 k ₀ -NAA | 81.08 | 81.07 | 80.12 | 82.14 | 79.7 | 82.37 | 81.08 | 1.06 |
| L05b ICP-QMS | 82.27 | 83.24 | 82.33 | 80.76 | 82.52 | 80.66 | 81.96 | 1.03 |
| L06 ICP-OES | 77.4 | 78.1 | 77.2 | 77.3 | 76.9 | 77.8 | 77.5 | 0.4 |
| L07 k ₀ -NAA | 89.0 | 87.0 | 85.0 | 88.0 | 88.0 | 86.0 | 87.2 | 1.5 |
| L09 ICP-QMS | 81.87 | 84.72 | 82.58 | 81.85 | 81.14 | 79.55 | 81.95 | 1.70 |
| L10 ICP-OES | 73.9 | 68.6 | 75.1 | 68.9 | 72.6 | 73.3 | 72.1 | 2.7 |
| L11 K ₀ -INAA | 81.4 | 80.8 | 82.5 | 81.0 | 81.8 | 80.8 | 81.4 | 0.7 |
| L11 FAAS | 80.2 | 80.2 | 78.7 | 79.0 | 79.4 | 79.4 | 79.5 | 0.6 |
| L11 ICP-QMS | 78.5 | 79.5 | 78.4 | 80.8 | 78.7 | 80.4 | 79.4 | 1.0 |

| Excluded results ^a | | | | | | | | |
|-------------------------------|------|------|-------|------|-------|-------|-------|------|
| L07 ICP-QMS | 88.9 | 83.7 | 133.0 | 82.2 | 135.5 | 130.3 | 108.9 | 26.4 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



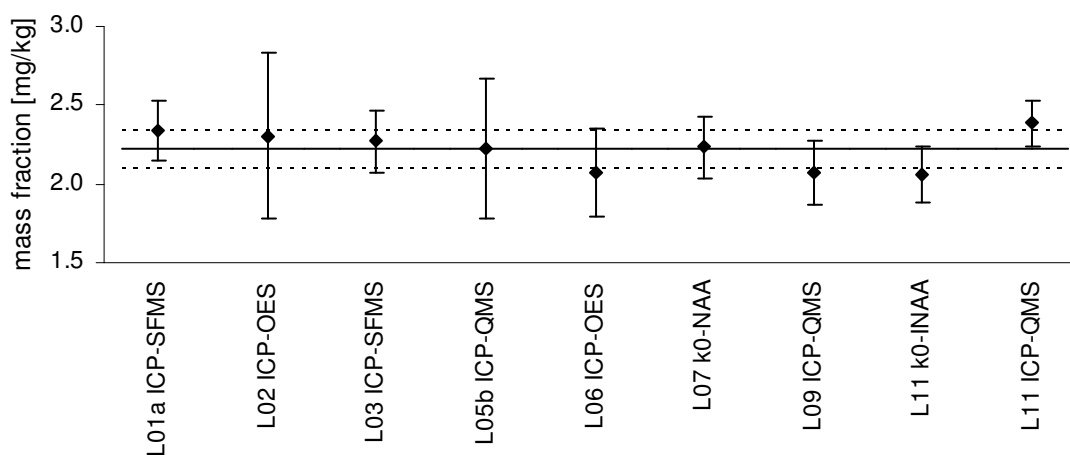
ERM-CD281, Mo

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|--------------------------|---------------------------------|-------|-------|-------|-------|-------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 2.34 | 2.29 | 2.33 | 2.44 | 2.34 | 2.28 | 2.34 | 0.06 |
| L02 ICP-OES | 2.424 | 2.324 | 2.300 | 2.423 | 2.256 | 2.107 | 2.306 | 0.118 |
| L03 ICP-SFMS | 2.258 | 2.269 | 2.240 | 2.239 | 2.301 | 2.320 | 2.271 | 0.033 |
| L05b ICP-QMS | 2.219 | 2.240 | 2.209 | 2.245 | 2.196 | 2.270 | 2.230 | 0.027 |
| L06 ICP-OES | 2.15 | 2.17 | 2.01 | 2.04 | 2.03 | 2.04 | 2.07 | 0.07 |
| L07 k ₀ -NAA | 2.2 | 2.2 | 2.2 | 2.2 | 2.3 | 2.3 | 2.2 | 0.1 |
| L09 ICP-QMS | 2.03 | 2.11 | 2.10 | 2.07 | 2.10 | 2.02 | 2.07 | 0.04 |
| L11 k ₀ -INAA | 2.15 | 2.04 | 2.17 | 2.04 | 2.00 | 1.97 | 2.06 | 0.08 |
| L11 ICP-QMS | 2.43 | 2.37 | 2.31 | 2.45 | 2.47 | 2.30 | 2.39 | 0.07 |

| Excluded results ^a | | | | | | | | |
|-------------------------------|------|------|------|------|------|------|------|------|
| L07 ICP-QMS | 2.62 | 2.24 | 2.38 | 2.70 | 2.38 | 2.79 | 2.52 | 0.22 |
| L10 ET-AAS | 1.80 | 1.60 | 1.60 | 1.78 | 1.67 | 1.74 | 1.70 | 0.09 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

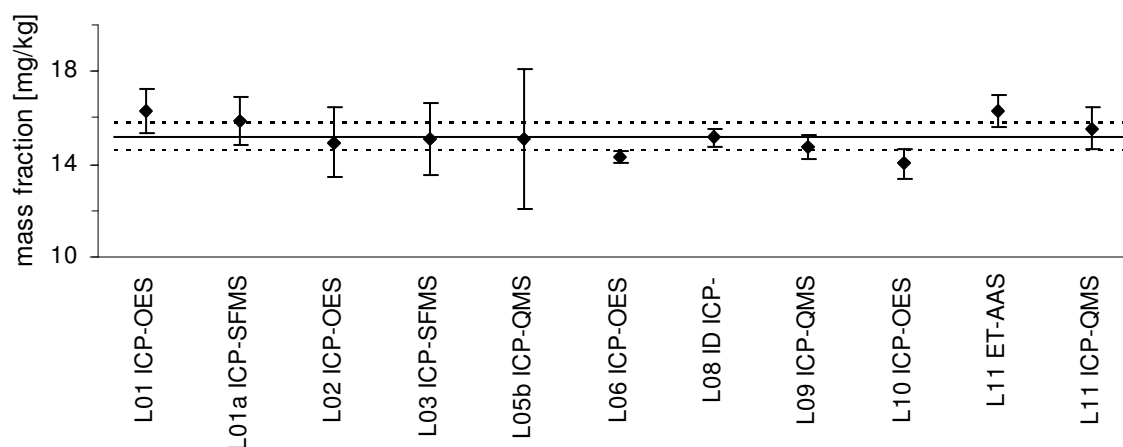


ERM-CD281, Ni

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01 ICP-OES | 15.9 | 16.2 | 16.0 | 16.8 | 16.4 | 16.5 | 16.3 | 0.3 |
| L01a ICP-SFMS | 16.0 | 15.5 | 15.8 | 16.4 | 16.0 | 15.6 | 15.9 | 0.3 |
| L02 ICP-OES | 14.926 | 14.873 | 15.049 | 15.103 | 14.934 | 14.838 | 14.954 | 0.102 |
| L03 ICP-SFMS | 14.91 | 15.15 | 14.72 | 14.80 | 15.46 | 15.56 | 15.10 | 0.35 |
| L05b ICP-QMS | 15.24 | 15.22 | 14.98 | 15.02 | 15.17 | 15.07 | 15.12 | 0.11 |
| L06 ICP-OES | 13.9 | 14.8 | 14.3 | 14.5 | 14.4 | 13.9 | 14.3 | 0.4 |
| L08 ID ICP-QMS | 15.219 | 15.126 | 15.662 | 14.714 | 15.293 | 14.809 | 15.137 | 0.344 |
| L09 ICP-QMS | 15.22 | 15.54 | 14.94 | 14.49 | 14.28 | 13.97 | 14.74 | 0.60 |
| L10 ICP-OES | 12.99 | 13.96 | 14.46 | 14.03 | 14.93 | 13.81 | 14.03 | 0.65 |
| L11 ET-AAS | 16.9 | 16.4 | 15.7 | 16.9 | 16.2 | 15.7 | 16.3 | 0.5 |
| L11 ICP-QMS | 15.6 | 15.4 | 16.0 | 15.0 | 15.7 | 15.6 | 15.6 | 0.3 |
| Excluded results ^a | | | | | | | | |
| L07 k ₀ -NAA | < 950 | < 950 | < 700 | < 700 | < 600 | < 600 | | |
| L07 ICP-QMS | 20.1 | 17.2 | 16 | 20.3 | 15.8 | 19 | 18.1 | 2.0 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



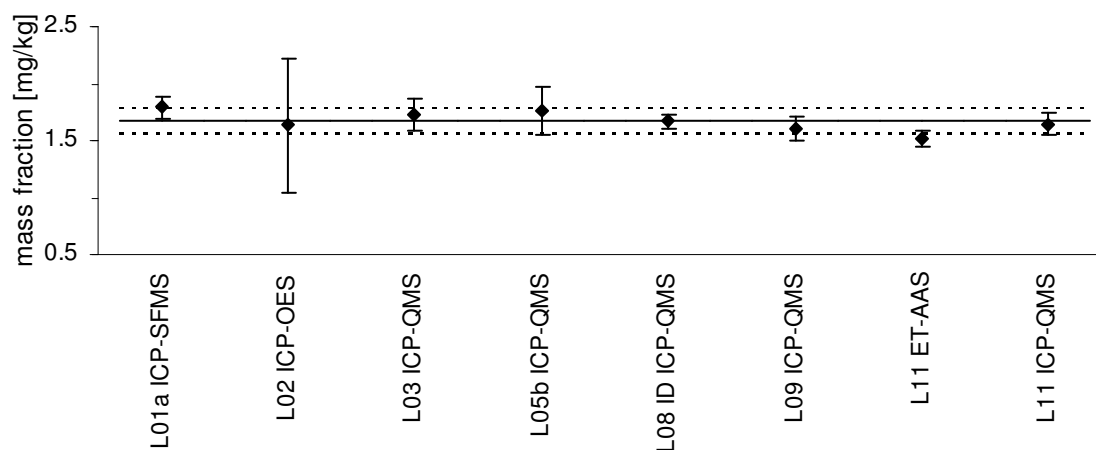
ERM-CD281, Pb

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-----------------|---------------------------------|-------|-------|-------|-------|-------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 1.79 | 1.76 | 1.80 | 1.83 | 1.79 | 1.78 | 1.79 | 0.02 |
| L02 ICP-OES | 1.639 | 1.566 | 1.624 | 1.699 | 1.698 | 1.577 | 1.634 | 0.057 |
| L03 ICP-QMS | 1.665 | 1.738 | 1.653 | 1.745 | 1.811 | 1.736 | 1.725 | 0.058 |
| L05b ICP-QMS | 1.734 | 1.802 | 1.754 | 1.764 | 1.777 | 1.720 | 1.759 | 0.030 |
| L08 ID ICP-QMS | 1.720 | 1.656 | 1.719 | 1.617 | 1.591 | 1.723 | 1.671 | 0.058 |
| L09 ICP-QMS | 1.658 | 1.645 | 1.636 | 1.636 | 1.533 | 1.533 | 1.607 | 0.058 |
| L11 ET-AAS | 1.66 | 1.54 | 1.45 | 1.62 | 1.38 | 1.46 | 1.52 | 0.11 |
| L11 ICP-QMS | 1.78 | 1.62 | 1.59 | 1.65 | 1.61 | 1.64 | 1.65 | 0.07 |

| Excluded results ^a | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| L01 ICP-OES | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 | | |
| L07 ICP-QMS | 2.02 | 1.72 | 1.78 | 3.50 | 1.76 | 2.16 | 2.16 | 0.68 |
| L10 ET-AAS | 2.164 | 2.365 | 1.795 | 2.227 | 1.919 | 2.047 | 2.086 | 0.209 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

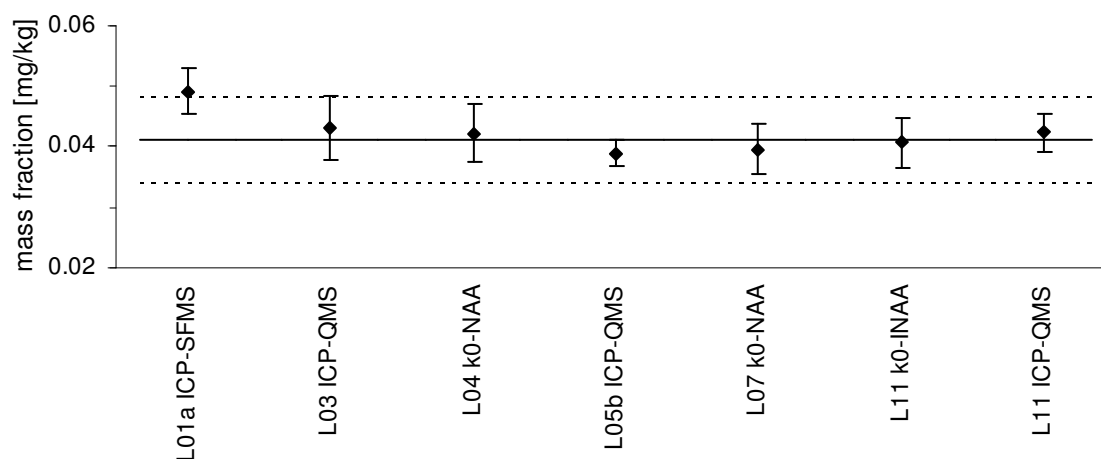


ERM-CD281, Sb

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 0.0497 | 0.0486 | 0.0505 | 0.0510 | 0.0466 | 0.0485 | 0.0492 | 0.0016 |
| L03 ICP-QMS | 0.0445 | 0.0421 | 0.0443 | 0.0427 | 0.0414 | 0.0442 | 0.0432 | 0.0013 |
| L04 k ₀ -NAA | 0.0424 | 0.0450 | 0.0358 | 0.0419 | 0.0443 | 0.0444 | 0.0423 | 0.0034 |
| L05b ICP-QMS | 0.038 | 0.040 | 0.040 | 0.037 | 0.040 | 0.039 | 0.039 | 0.001 |
| L07 k ₀ -NAA | 0.042 | 0.037 | 0.037 | 0.042 | 0.039 | 0.041 | 0.040 | 0.002 |
| L11 k ₀ -INAA | 0.044 | 0.041 | 0.037 | 0.042 | 0.039 | 0.041 | 0.041 | 0.002 |
| L11 ICP-QMS | 0.043 | 0.043 | 0.042 | 0.042 | 0.042 | 0.042 | 0.042 | 0.001 |
| Excluded results ^a | | | | | | | | |
| L02 AFS | 0.025 | 0.124 | 0.151 | 0.017 | 0.264 | 0.358 | 0.157 | 0.134 |
| L07 ICP-QMS | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | | |
| L10 HG-AFS | 0.70 | 0.85 | 0.91 | 1.03 | 1.02 | 0.36 | 0.81 | 0.25 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



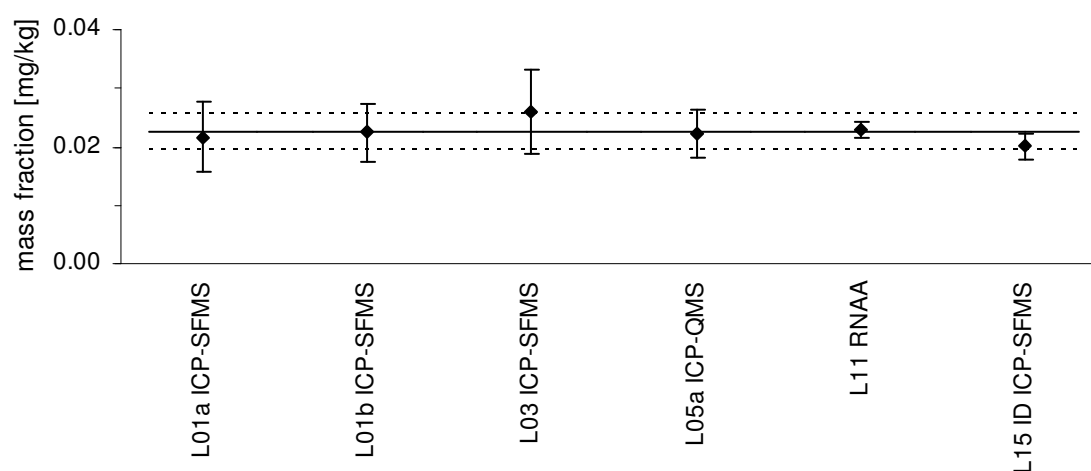
ERM-CD281, Se

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-----------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 0.0225 | 0.0205 | 0.0219 | 0.0208 | 0.0208 | 0.0236 | 0.0217 | 0.0012 |
| L01b ICP-SFMS | 0.0232 | 0.0246 | 0.0214 | 0.0223 | 0.0224 | 0.0205 | 0.0224 | 0.0014 |
| L03 ICP-SFMS | 0.0302 | 0.0258 | 0.0246 | 0.0260 | 0.0250 | 0.0241 | 0.0260 | 0.0022 |
| L05a ICP-QMS | 0.022 | 0.022 | 0.022 | 0.025 | 0.022 | 0.020 | 0.022 | 0.002 |
| L11 RNAA | 0.0223 | 0.0220 | 0.0223 | 0.0235 | 0.0232 | 0.0243 | 0.0229 | 0.0009 |
| L15 ID ICP-SFMS | 0.0200 | 0.0195 | 0.0202 | 0.0204 | 0.0198 | 0.0203 | 0.0200 | 0.0003 |

| Excluded results ^a | | | | | | | | |
|-------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|
| L01 AFS | 0.166 | 0.154 | 0.206 | 0.121 | 0.091 | 0.155 | 0.149 | 0.039 |
| L02 AFS | 0.108 | 0.154 | 0.011 | 0.154 | 0.018 | 0.026 | 0.079 | 0.068 |
| L06 ICP-SFMS | 0.02734 | 0.02661 | 0.02735 | 0.03610 | 0.03001 | 0.03042 | 0.02964 | 0.00353 |
| L07 k ₀ -NAA | < 0.2 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | | |
| L07 ET-AAS | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | | |
| L08 ID ICP-SFMS | 0.037 | 0.034 | 0.034 | 0.040 | 0.027 | 0.025 | 0.033 | 0.006 |
| L10 ET-AAS | 0.17 | 0.19 | 0.19 | 0.17 | 0.16 | 0.23 | 0.19 | 0.03 |
| L12 ICP-QMS | 0.63 | 0.65 | 0.71 | 0.66 | 0.64 | 0.73 | 0.67 | 0.04 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

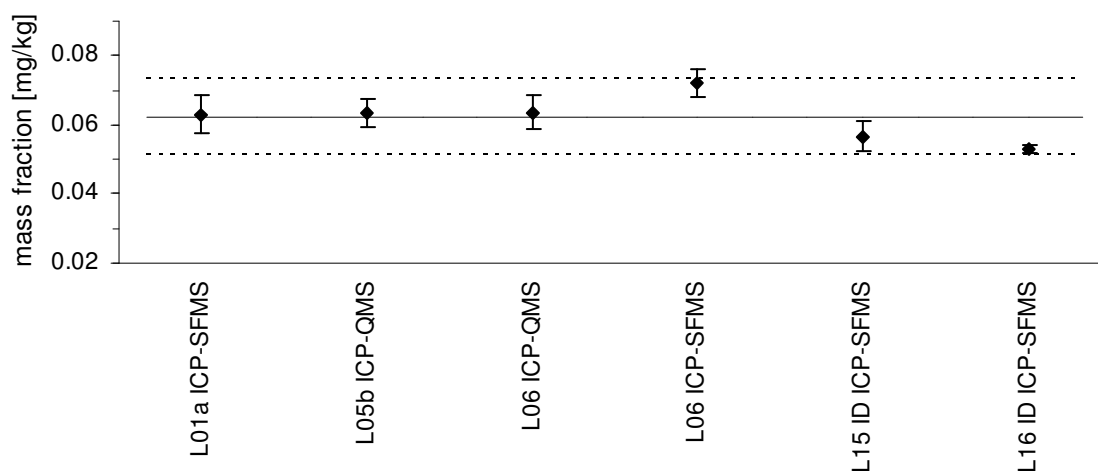


ERM-CD281, Sn

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|-------------------------------|---------------------------------|---------|---------|---------|---------|---------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01a ICP-SFMS | 0.0629 | 0.0631 | 0.0649 | 0.0633 | 0.0624 | 0.0617 | 0.0631 | 0.0011 |
| L05b ICP-QMS | 0.064 | 0.063 | 0.060 | 0.066 | 0.065 | 0.061 | 0.063 | 0.002 |
| L06 ICP-QMS | 0.06095 | 0.06194 | 0.06402 | 0.06825 | 0.06362 | 0.06304 | 0.06364 | 0.00253 |
| L06 ICP-SFMS | 0.07485 | 0.07047 | 0.07371 | 0.07151 | 0.07056 | 0.07083 | 0.07199 | 0.00185 |
| L15 ID ICP-SFMS | 0.0523 | 0.0625 | 0.0598 | 0.0565 | 0.049 | 0.0602 | 0.0567 | 0.0052 |
| L16 ID ICP-SFMS | 0.05610 | - | 0.05582 | 0.04946 | 0.05118 | 0.05289 | 0.05309 | 0.00289 |
| Excluded results ^a | | | | | | | | |
| L02 ICP-OES | 0.066 | 0.102 | 0.013 | 0.104 | 0.223 | -0.058 | | |
| L03 ICP-SFMS | 0.0505 | 0.0437 | 0.0591 | 0.0524 | 0.0612 | 0.0688 | 0.0560 | 0.0089 |
| L07 k ₀ -NAA | < 10 | < 10 | < 15 | < 16 | < 11 | < 11 | | |
| L07 ET-AAS | 0.23 | 0.16 | 0.27 | 0.30 | 0.11 | 0.12 | 0.20 | 0.08 |
| L10 ET-AAS | 8.415 | 7.879 | 6.822 | 8.049 | 8.273 | 9.122 | 8.093 | 0.756 |
| L12 ICP-QMS | 0.10 | 0.09 | 0.08 | 0.07 | 0.08 | 0.08 | 0.08 | 0.01 |
| L13 ICP-QMS | 0.215 | 0.116 | 0.077 | 0.078 | 0.090 | 0.200 | 0.129 | 0.062 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



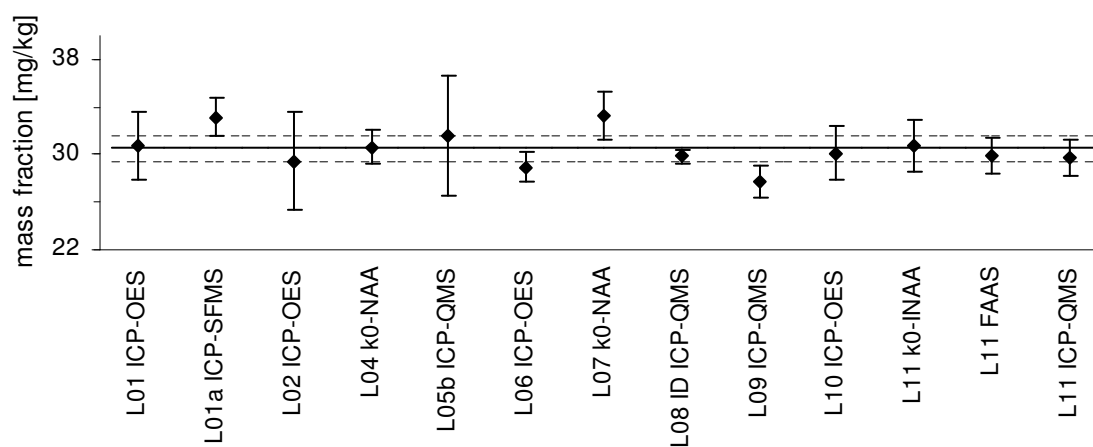
ERM-CD281, Zn

| Lab-method code | Individual results ^a | | | | | | \bar{x} | s |
|--------------------------|---------------------------------|--------|--------|--------|--------|--------|-----------|---------|
| | [mg/kg] | | | | | | [mg/kg] | [mg/kg] |
| L01 ICP-OES | 30.3 | 30.6 | 30.8 | 31.3 | 30.9 | 30.8 | 30.8 | 0.3 |
| L01a ICP-SFMS | 33.2 | 32.1 | 33.2 | 33.5 | 33.7 | 33.3 | 33.2 | 0.6 |
| L02 ICP-OES | 29.699 | 29.484 | 29.627 | 29.207 | 29.601 | 29.047 | 29.444 | 0.260 |
| L04 k ₀ -NAA | 30.502 | 30.088 | 31.128 | 30.522 | 30.957 | 30.452 | 30.608 | 0.376 |
| L05b ICP-QMS | 31.8 | 32.0 | 31.8 | 31.4 | 31.6 | 31.1 | 31.6 | 0.3 |
| L06 ICP-OES | 28.8 | 29.7 | 29.1 | 28.9 | 28.6 | 28.7 | 29.0 | 0.4 |
| L07 k ₀ -NAA | 34.0 | 34.0 | 32.0 | 34.0 | 33.0 | 33.0 | 33.3 | 0.8 |
| L08 ID ICP-QMS | 30.47 | 30.26 | 30.69 | 29.23 | 29.78 | 28.55 | 29.83 | 0.82 |
| L09 ICP-QMS | 29.64 | 29.77 | 26.78 | 29.20 | 25.94 | 25.24 | 27.76 | 2.01 |
| L10 ICP-OES | 29.5 | 27.9 | 31.3 | 28.5 | 29.8 | 33.8 | 30.1 | 2.1 |
| L11 k ₀ -INAA | 30.7 | 30.9 | 30.3 | 30.9 | 30.7 | 30.9 | 30.7 | 0.2 |
| L11 FAAS | 30.6 | 29.0 | 30.4 | 30.3 | 29.5 | 30.0 | 30.0 | 0.6 |
| L11 ICP-QMS | 29.3 | 29.9 | 29.4 | 30.7 | 29.3 | 29.8 | 29.7 | 0.5 |

| Excluded results ^a | | | | | | | | |
|-------------------------------|------|------|------|------|------|------|------|------|
| L07 ICP-QMS | 69.6 | 44.6 | 69.1 | 43.7 | 70.9 | 67.3 | 60.9 | 13.0 |

^a: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



European Commission

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Title: Certification of the mass fractions of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn in rye grass, ERM[®]-CD281

Author(s): E.Perez Przyk, A.Held

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Abstract

This report describes the preparation and certification of the rye grass Certified Reference Material (CRM) ERM-CD281. This CRM replaces the exhausted predecessor BCR-281. ERM-CD281 was processed and certified by the European Commission, Directorate General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

ERM-CD281 has been certified for its content of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn.

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

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